

AN INVESTIGATION OF THERMAL  
TRANSIENTS USING THERMISTORS

257

By  
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## CHAPTER I

### INTRODUCTION

The reason for determining properties of physical systems with greater precision is not only for the precision itself and the possible ensuing betterment of accuracy, but also to detect errors in order to improve the interpretation and the use of systems in which there is interest. The determination and use of thermal gradients or transients, particularly in calorimetry, is of primary theoretical and practical importance to the modern physical sciences. The use of the word transient is explicit in this work since the actual measurements (at any conceivable limits) are of short duration. The determination of the relation of various primary thermal transients to standard temperature values and the maintenance of standard calorimetric substances are basic tasks performed by most national physical laboratories. According to the quantum theory the present concept of heat flow and resultant changes provides for discrete quantities of energy to be transferred in a process as contrasted to a continuous flow. Within the scope and physical limitations of the present

work, the above concept interferes in no manner with the handling of the material as though it were uniform and/or variably continuous.

No detailed review or bibliography on calorimetry is undertaken herein since there are numerous and sufficient sources available. Outstanding among the modern works are the monographs of White<sup>1</sup> and Swietoslawski,<sup>2</sup> the limited survey works of Reilly and Ray<sup>3</sup> and Weissburger<sup>4</sup> and the texts of Barton,<sup>5</sup> Cork<sup>6</sup> and Weber.<sup>7</sup> Further, no extensive bibliography is presented on instrumentation since specific details and references will be referred to in the pertinent following sections.

A survey of modern precision calorimetry shows a decided preference for adiabatic (no heat exchange) methods, which have been developed by Osborn and co-workers<sup>8</sup> to a high degree of refinement. The improvements of these adiabatic methods have caused, in part, the so-called cruder methods (p. 155)<sup>1</sup> to utilize more sensitive instruments. These apparently cruder methods are popular, as evidenced by the increasing number of investigators using them, because of their greater rapidity of measurement, the improved material available and advances in the design of equipment. In particular, the methods, other than adiabatic, have

tended toward radiative and cooling methods (including the method of mixtures) to which Newton's so-called (according to Cork) law of cooling has been applied. There is some apparent conflict as to the interpretation of the empirical law of Newton, particularly with regard to the range of temperature difference over which it is applicable.

Indeed, Cork (p. 159)<sup>6</sup> refers to an anonymous article entitled "Calor," in the Philosophical Transactions of the Royal Society, Vol. XXII, pp. 827-829, (1710), which is believed to have been written by Newton. This article places no explicit limit on the temperature change of a cooling body other than that the body be exposed to a draft. The article then states that the temperature decreases geometrically with respect to a lower reference temperature. To quote from a translation<sup>9</sup>,

"For the heat which hot iron communicates to cold bodies in contact with it in a given space of time is the heat which the iron loses in a given time, or the total heat of the iron. Therefore, if the times of cooling be assumed equal, the heats will be in geometric proportion, and, consequently, may be easily determined by the table of logarithms.

. . . . .

Then, taking account of the fact that



the excess of the heats of iron and the solidifying particles over the heat of the atmosphere had been established, by means of the thermometer, as being in geometric progression, whereas the times are in arithmetic progression, all the heats became clear."

The present work attempted to reproduce the conditions purportedly stated and used by Newton and to provide better means for physical systems including those undergoing rapid changes. Physically, if there were only one time at which one could make an observation on a given system this so-called "one shot" should be as close to perfect as one can obtain. A series of "one shot" observations under proper control constitutes valid data, and if the series is continuous with uniform control, there is the least question with regard to the validity of the observations. Restricting considerations to those of thermal processes, the general requirements, which are within the limitations of the equipment used, are:

1. Precise and accurate detection and/or measurement of electrical resistance or temperature.
2. Use of devices which if not stable are determined to be uniformly variable.

In the present work the above requirements are met in part by the sensing device which is a small thermally sensitive resistor known as a "thermistor." The thermistor is used as a part of an arm in a Wheatstone bridge whose null is detected by an electronic amplifier. This detecting and measuring device has a relatively high sensitivity with regard to the thermistor and its rate of change. With such equipment it should be possible to detect extremely rapid or extremely small thermal transients and to measure changes of heat content within a nominal range.

The purpose of this investigation is to attempt, by the use of the method and technique indicated previously, the measurement and the determination of the heat capacities of  $\alpha$ -pinene,  $\beta$ -pinene, 1-limonene and dipentene.

## CHAPTER II

### THEORETICAL CONSIDERATIONS

#### Selection of Method

As was previously stated in the introduction, the recent authorities and the standard laboratories have tended to favor adiabatic methods for calorimetry. The reason, as detailed and examined by White, is due chiefly to the diminution of the thermal head in the fundamental equation for temperature loss

$$t\left(\frac{\partial T}{\partial t}\right)_c = \Delta\theta t \quad (I)$$

where  $T$  in the above equation is temperature;  $t$  is the time;  $c$ , the heat capacity over a small range;  $\theta$  is the thermal head or temperature difference between the calorimeter and its environment; and  $A$ , the thermal leakage modulus which is the equivalent of the multiplier of the thermal head. Additional support of the adiabatic method, as stated by Swietoslowski,<sup>2</sup> is obtained through strict controls on heat gains and losses as well as elegant methods for the evaluation of the system.

In the recent work on calorimetric systems by the U.S. Bureau of Standards,<sup>8</sup> vacuum-insulated sys-

tems have been used predominantly since conduction and convection effects are reduced to the minimum. The foregoing method requires extensive instrumentation and testing in order to evaluate the system under investigation.

In view of the above it was decided that an especially versatile method would be desirable in the present investigation. According to Swietoslowski (pp. 2-9 and Chapter XI),<sup>2</sup> an attempt to classify the process to be investigated should be made before the method is chosen. The process reported in this dissertation may be classified as one of short duration, since any process of short duration may be treated by summative steps.

A vacuum jacketed or Dewar type calorimeter would appear to satisfy the foregoing classification of Swietoslowski if totally immersed in an isothermal bath. A totally immersed Dewar in a constant temperature system is considered to meet the thermal damping requirements of a multi-jacketed system which appears to be preferred by Swietoslowski. The size of the sample is usually a matter of convenience, limited only by the quantity of material available and the volume effect inside the Dewar.<sup>10</sup> White states that a Dewar has less effect from lags and also can be stirred more slowly. In addition to these

factors the constant,  $\theta$ , in equation (I) may be treated more crudely and the variation in  $A$ , in the same equation, tends to be smaller.

Any device inserted into a system to measure certain of the system's properties will cause a change in the system. This change may appear through the system's energy capacity or some rate of change of the system. All energy properties involve a balance or a rate of transfer. Both are more susceptible to interference. It is not planned to investigate the effect of interferences, but rather to bear them in mind and to minimize them as much as possible. The difficulty of measuring energy or its extraction is not easily solved. In this work the final solution to such difficulty has not been reached, but it is hoped that a progressive step has been made. A method of approach, capable of great extension, has been attempted which could find greater application.

The following derivation of Newton's law of cooling involves certain limitations. It is taken essentially from Weber (p. 101),<sup>7</sup> who made the derivation from the Stefan Boltzman radiation law, in the same manner as many others have used. For a black body the total radiance  $R_b$  is defined as

$$R_b = \sigma T^4 \quad (\text{II})$$

where  $\sigma$  is the Stefan Boltzman constant and  $T$  is the absolute temperature. The net rate of energy loss

$\frac{dQ}{dt}$  for small temperature differences, is

$$\frac{dQ}{dt} = A(R_1 - R_2) \approx A\sigma(T_1^4 - T_2^4) \quad (\text{III})$$

$$= A\sigma(T_1 - T_2)(T_1 + T_2)(T_1^2 + T_2^2) \quad (\text{IV})$$

When the higher temperature  $T_1 \approx T_2$  the summative terms are practically constant and

$$\frac{dQ}{dt} = A' (T_1 - T_2) \quad (\text{V})$$

where  $A$  is a constant of proportionality and the primed letter is

$$A' = \sigma A(T_1 + T_2)(T_1^2 + T_2^2) \quad (\text{VI})$$

If the heat capacity  $c$  (and all other influencing factors) are approximately constant within the range considered, the rate of cooling  $\frac{dT}{dt}$  is proportional.

to  $\frac{dQ}{dt}$  as:

$$\frac{dT}{dt} = \frac{1}{mc} \frac{dQ}{dt} = \frac{1}{mc} A'(T_1 - T_2) = A''\Delta T \quad (\text{VII})$$

where  $m$  is the mass of the body and  $A'' = \frac{A'}{mc}$ . The above approximate equation depends mathematically upon  $T_1 \cong T_2$  and is based chiefly upon radiative properties. This equation is one of the forms for which data are taken to supply the variety of calorimetric values in use.

The foregoing derivation agrees with the principles, intents and practices delineated by both White<sup>1</sup> and Swietoslowski.<sup>2</sup> However, if we rephrase explicitly the quotation on page 3, ascribed to Newton, it may be reduced to:

"The excess of temperature of a cooling body is in geometric progression while the time of such change is in arithmetic progression."

If, as Newton stated, the body must cool in a forced draft, then, if the draft be constant in temperature, the primary influence would depend in large part upon the ability of the body and draft to transfer heat. Both Barton (pp. 31-32)<sup>5</sup> and Weber (p. 101)<sup>7</sup> state that in the complex case conduction, convection and radiation are important. It is not intended in this work to present the

details of such a complex case. Rather, the data were taken in such a way so that future data, when taken in comparable manner, may allow greater resolution of the entire cooling curve. The present work contains data which may be used to test the validity of the foregoing in a practical manner.

From the above it is seen that the attack on the problem was made from a reasonable premise; but it may prove to be different from the usually accepted or understood methods. A further variation in the experimental method with an unsilvered Dewar might provide a more detailed and a better understanding of the problems of range, cooling, energy transfer and numerous allied variables.

#### Heat Capacity Determination

The methods of heat capacity determination are adequately reviewed, derived and discussed by such writers as Barton (Chapter II),<sup>5</sup> Cork (pp. 41, 71 and 93)<sup>6</sup> and Weber (pp. 171-187 and p. 323).<sup>7</sup> In view of the previous discussion this course of investigation has been restricted to one with a Dewar type flask in a constant temperature bath. The choice of method leads to the use of a technique similar to that of the radiation or cooling method of analysis. Numerous investigations have utilized one of these



methods. Among recent reports, the thermal leakage method at constant pressure technique by Spear,<sup>11</sup> is representative of the radiation method. Certain features of this article appear to approach the requirements of this investigation. A comparison of the cooling method discussed by Cork (pp. 63-64)<sup>6</sup> with that of Barton (pp. 35-36)<sup>5</sup> reveals a possibility for much wider application of the cooling method. This wider application is defined, according to Barton, through the function  $f(T)$ , and is mentioned by Weber (p. 101).<sup>7</sup> This function  $f(T)$ , as expressed, might possibly be investigated through variations, such as rate of the cooling method. If analysis of data should be complex, a series solution might be used to evaluate  $f(T)$ . The series might, in turn, be approximated to a certain number of terms by an orthogonal polynomial which could rapidly reduce the data to equation form. Utilizing Barton's thermal leakage formula (pp. 35-36)<sup>5</sup> rearranged as follows:

$$\frac{C_a + c_a M_a}{\Delta t_a} = \frac{\bar{C}_b + c_b M_b}{\Delta t_b} \quad (\text{VIII})$$

where  $C$  equals the thermal capacity of vessel and associated apparatus in gram calories per °C,  $c$  equals the specific heat of liquid contents of vessel in calories per gram per °C,  $M$  equals the mass of

liquid contents in grams, and  $t$  equals the time of heating or cooling in seconds. The subscripts  $a$  and  $b$  refer to two different systems.

Since only one calorimeter is used, the surface and area are assumed uniform in the range used, and

$$C_a = C_b.$$

For the present work these were assumed to be constant since the same container and volume were used throughout,

and 
$$\frac{\bar{C}_a + c_a M_a}{\Delta t_a} = \frac{\bar{C}_b + c_b M_b}{\Delta t_b}$$

from which

$$c_b = \frac{\bar{C}_a(t_b - t_a) + c_a M_a \Delta t_b}{M_b \Delta t_a} \quad (\text{IX})$$

This yields the heat capacity in terms of uniform increments of temperature at identical comparison temperatures.

If a correctional factor is needed for evaporation we may subtract such appropriate factors  $E_a$  and  $E_b$  from each side of equation (IX) and obtain

$$\bar{C}_b = \bar{C}_a \left( \frac{\Delta t_b}{\Delta t_a} - 1 \right) + (C_a M_a - E_a) \frac{\Delta t_b}{\Delta t_a} - \Delta t_b E_b \quad (\text{X})$$

The above formula may be used to test for the effects of evaporation or condensation by using different volumes of material in the calorimeter for the same exposed surface area of liquid.

### Thermistor Factors

The outstanding work of Becker et al.<sup>12</sup> is responsible for the elucidation of the theory and the increasing use of thermistors as an electrical circuit component and particularly as a temperature sensing device. Using the relations given by Becker et al. (pp. 6, 7 and 10)<sup>12</sup> and computing from estimated capacities and volumes of material to be investigated with the requirements of a wide range, the sensing system appears to fit the Western Electric type 14A or 6014A pair thermistor.<sup>13, 14</sup> The choice for the 6014A pair thermistor was governed by the following:

- (1) the small size 0.10 x 0.6 1 inches,
- (2) large temperature coefficient,  
 $\alpha$  in  $\%/^{\circ}\text{C}$  of nominal resistance,
- (3) a moderate power dissipation constant,  
 $\phi$ , in milliwatts/ $^{\circ}\text{C}$ ,
- (4) the maximum temperature usable, up to  
 approximately  $300^{\circ}\text{C}$ , and
- (5) a reasonable thermal time constant,  
 defined as the time to reach 63%  
 of a given resistance value under  
 given conditions.

Since the resistance of the thermistor is power-sensitive it is necessary to have a power level

below the value which would cause the smallest percentage/error in the accuracy desired at a maximum resistance value. This may be determined by the definition on page 6 of Becker et al.<sup>12</sup>

$$\begin{aligned} p &= \delta/\mathcal{L} \times \% \text{ base} \\ &= \delta/\mathcal{L} \times 10^2 \text{ in parts/100} \end{aligned} \quad (\text{XI})$$

where p, the power sensitivity, is the number of watts dissipated before the resistance decreases one percent.

From Table III, page 10, of Becker et al.,<sup>12</sup>  $\delta = 1$  milliwatt for air and  $= 3.3 \text{ to } 4.5 \times 10^{-2}$

$$\begin{aligned} p &= 1 \times 10^{-3} \times 4.4 \\ &= 2.25 \times 10^{-4} \text{ watt/}^\circ\text{C.} \end{aligned}$$

This is the power necessary under very poor conditions of thermal transfer for one percent precision. Since the liquids used have a thermal transfer much greater than that of air, they were stirred adequately to insure as uniform a temperature as possible. The value taken for a thermal time-constant from Western Electric Tentative Information Sheet 6014A,B was intermediate between that of oil and water to have a multiplier value of

$$\begin{aligned} 4.3 \times 10^3 &= 43 \times 2.25 \times 10^{-4} \text{ watt/}^\circ\text{C} \\ \text{NP} &= 9.67 \times 10^{-3} \text{ watt/}^\circ\text{C} \end{aligned} \quad (\text{XII})$$

for maximum dissipatable power for a one percent precision. For greater precision for each percent factor change, multiply

$$NP \times F \quad (\text{XIII})$$

where F is the factor to convert 100 percent to 1000 percent, 10,000 percent, etc. to obtain the power level required for a given precision as a sensing element. Dowell, in a recent publication,<sup>13</sup> details some of the design factors and gives a very fine bibliography of references.

Included in Dowell's article are data for a thermal time-constant which must be approximated since rate transfer and power level are again involved. In this consideration the thermal time-constant can be considered to be a percentage change factor which is the reciprocal of  $\phi$

$$\Delta T_t = \frac{K}{\phi} \quad (\text{XIV})$$

where  $\Delta T_t$  is the time required to reach 63 percent of the resistance value at temperature T under given power level conditions.

If one desires to calibrate the thermistor over a short temperature range the formula given on page 3 by Becker et al.<sup>12</sup> is,

$$R_t = R_0 e^{\frac{B}{T}} - \frac{B}{T_0} \quad (\text{XV})$$

where

$R_t$  is the resistance at  $T$

$R_0$  is the resistance at  $T_0$

$B$  is assumed to be a constant

and  $e = 2.71828$

The above formula has been used extensively for short temperature ranges in investigations of moderate precision. A glance at Table II of the same article shows that  $B$  is not constant and that further mathematical operations may fit the data with greater precision. If  $B$  is assumed to be a constant one may calibrate and compute the necessary data over a small temperature range by means of equation XV.

#### Detection and Amplification Circuits

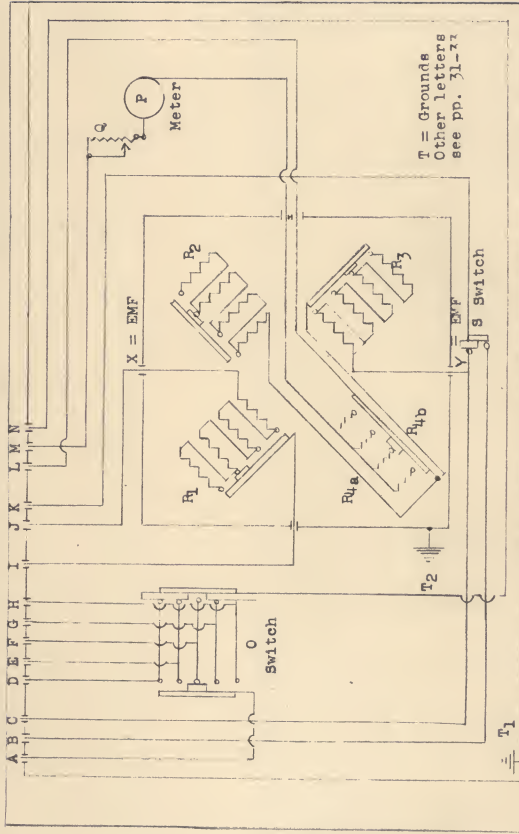
The most sensitive detection circuit capable of quick calibration is that of a Wheatstone bridge (see Figure 1). If, in Figure 1, the potential difference between  $x$  and  $y$  equals zero, then

$$I_1 R_1 = I_2 R_3 \quad (\text{XVI})$$

and

$$I_1 R_2 = I_2 R_4 \quad (\text{XVII})$$

where  $I$  is the current and  $R$  is the resistance in the numbered arms



SHIELDED BRIDGE AND SWITCH ASSEMBLY  
 Figure 1

But for equal potentials at x and y,  $I_1 = I_2$  and

$$\frac{R_1}{R_2} = \frac{R_3}{R_4} \quad (\text{XVIII})$$

By setting up three arms of such a system and an appropriate decade arm as the fourth, such a circuit may be calibrated and/or balanced. Along with such a decade arm may be included unknown resistances in series which may be evaluated by comparison with the decade by a simple proportion.

The electronic amplifier used for detection was a type CAOR50268 DC Amplifier, which is classified as Restricted Security Information. It is a chopper phase inversion type amplifier. There are references to similar ones in the bibliography of this report (15-17), and no further details will be given here.

#### Mathematical Treatment and Resolution of Data

The method of averages is used wherever no appreciable error is introduced into the results, or where graphical evaluations have been used. This is usually used for simple linear relations.

For all other data in which the original formula appears to be unsatisfactory, and if the precision warrants the computation, the orthogonal polynomials



of Section 72, pp. 265-275,<sup>18</sup> Milne may be used. Wherever these are used Milne's notation will be followed by literal transformations in the computations involved. No attempt is made in this work to delineate the properties other than the fact that one coordinate system must contain equally spaced points. This last condition was approximately met in all experimental work and will be apparent in later sections when used.

If it is desired to use the thermistor formula for greater precision, by means of the orthogonal polynomials, the fundamental equation, on page 3 of Becker et al.,<sup>12</sup> should be transformed as follows:

$$R = R_{\infty} e^{\frac{B}{T}} \quad (\text{XIX})$$

$$\ln \frac{R}{R_{\infty}} = \frac{B}{T} \quad (\text{XX})$$

$$1/\ln(R/R_{\infty}) = f(R) = T/B \quad (\text{XXI})$$

$$\text{now let} \quad f(R) = f(T) \quad (\text{XXII})$$

where  $T$  is in uniform increments and is in a form adaptable to the above mentioned polynomial solution.

Computations involving heat capacity data have been taken in such a manner that simply transformed or rearranged equations may be used. Specific

examples will be illustrated later wherever applicable. In some cases simple visual or tabular, where necessary, difference formulas are used for interpolation between given data values.

## CHAPTER III

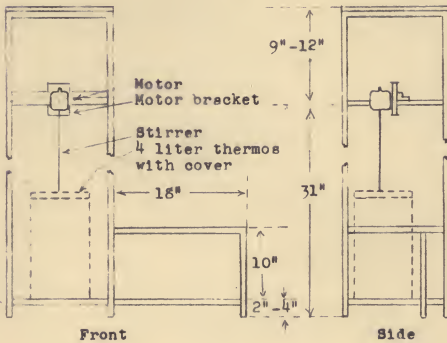
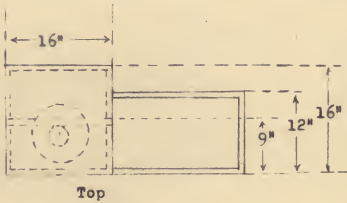
### APPARATUS AND MATERIEL

#### 1. Apparatus.

The support used to hold the various parts of the apparatus is a simple 1" x 1" angle iron frame as schematically diagramed in Figure 2. The high vertical stand was arranged to accommodate either reciprocating or rotary type stirrers. Any additional mounting could be made on the angle iron faces of the support by means of clamps. The top and bottom contained close-fitting aluminum plates which could be adapted for additional mountings.

The calorimeter stirrer was a double bladed, reverse-pitch, triple-segment propeller type made of glass. Each segment was mounted one inch above the other, and the entire assembly was positioned in the center of the Dewar approximately one-half inch above the bottom. After several motors had been tried an induction motor controlled by a Variac, both of which cause a minimum of electrical noise, proved most satisfactory.

The constant temperature bath (CTB) stirrer was a sixteen-bladed, Torrington, turbine-type stirrer bought from War Surplus. This was chucked on a glass



SUPPORT

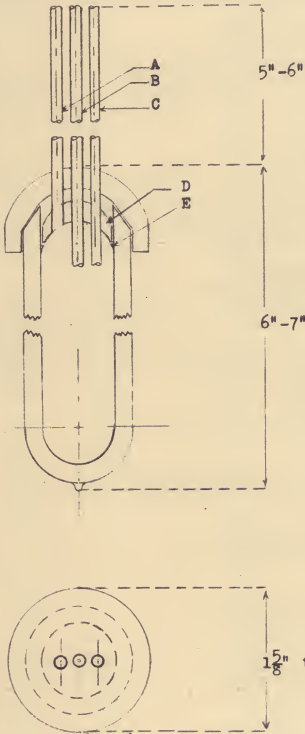
Figure 2 -

shaft driven by a geared motor controlled by a Variac. Although this motor was the best available for driving the stirrer, it caused a shift, when running, equivalent to 10-15 ohms in the null of the Wheatstone bridge detector. The stirrer proved to be most efficient for the equilibration of the constant-temperature bath. In all cases motors and other electrical devices with a minimum of noise in proximity to the electronic amplifier were chosen.

## 2. The Dewar Systems.

The constant-temperature bath consisted of a four-liter Thermos Pyrex type Dewar which was fitted with the calorimeter bracket and cover. All cemented type brackets proved unsatisfactory in use. The bracket used was a welded steel Y with positioning holes in one arm. This was placed with the Y toward the bottom of the Dewar. The lid, made of cypress, covered with aluminum foil contained appropriate holes for the stirrer, the Dewar leads and the platinum resistance thermometer.

The calorimeter was constructed as indicated in Figures 3 and 4. The technique of construction is somewhat unusual since the lightest-walled vessel obtainable was desired. A flow-sheet of operations details the steps used in constructing the Dewar parts.



### LEGEND

- A - Heater lead or pouring tube
- B - Stirrer tube
- C - Thermistor tube
- D - Condensation and spatter shield
- E - Support shoulder

Note: The maximum volume of calorimeter was built so as to not exceed 80 ml.

DEWAR TYPE CALORIMETER

Figure 3

# DIAGRAMMATIC FLOW SHEET

Figure 4

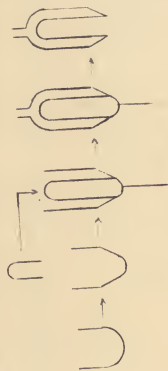
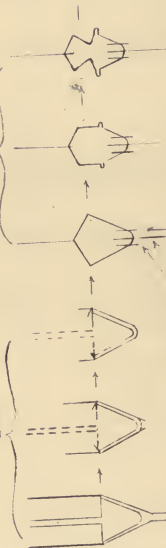


Figure 4a

III  
6-15

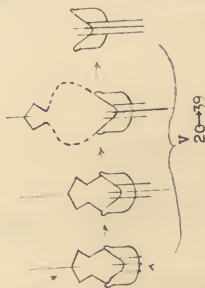
I\*  
1-4



IV  
15-19

\* Roman numerals refer to steps on Flow Sheet for Dewar Gap Construction.

Figure 4b



V  
20-39

# FLOW SHEET

## DEWAR CAP CONSTRUCTION

<u>STEP</u>	<u>PART DESCRIPTION</u>	<u>NO.</u>	<u>OPERATION</u>	<u>DETAIL</u>
I	Inner Cone	1	Draw tube	Form spindle
		2	Form shrink	Flame anneal
II	End Tubes	3	Draw open end	Form spindle
		4	Cut to length	Form spindle
III	Inner Cone Assembly	5	Olive compression	Readjust length
		6	Measure work distance	Blow inner tube mbs
		7	Seal center tube	Ream, true and center
		8	Seal side tube 1	Anneal
		9	Draw side tube	Ream, true and center
		10	Seal side tube 2	Anneal
		11	Draw side tube	Ream, true and center
		12	Anneal	Check seal on vacuum
		13	Check outer dome height	Set compression ring
		14	Set sag ring	Anneal
IV	Outer Dome Assembly	15	Draw tube	Adjust dome height
		16	Blow dome	Set flare ring
		17	Form spindle	Anneal
		18	Blow out bottom	
		19	Cut	
V	Dewar Cap Assembly	20	Set inner end tubes	Cut for outer dome assembly
		21	Rub outer dome assembly	Coflame anneal all steps
		22	Bulb center and side tubes	Adjust dome center and height
		23	Blow center tube	Tubulate true and seal
		24	Blow side tube 1	Tubulate true and seal
		25	Blow side tube 2	Tubulate true and seal
		26	Blow breather vent on dome	Tubulate and true
		27	Blow inner cone to outer dome	Shrink and cut excess
		28	Flame set edge	Anneal well
		29	Vacuum test	
VI	Silvering	30	Prepare stock solution	Rochelle salt 4 parts, cold H <sub>2</sub> O 14 parts
				Silver nitrate 1 part}
		31	Rinse with soluble tin salt and distilled H <sub>2</sub> O	Tin salt equivalent to .001%
		32	Put volumetric of stock in Dewar	Set in hot H <sub>2</sub> O
		33	Dry, evacuate and seal	



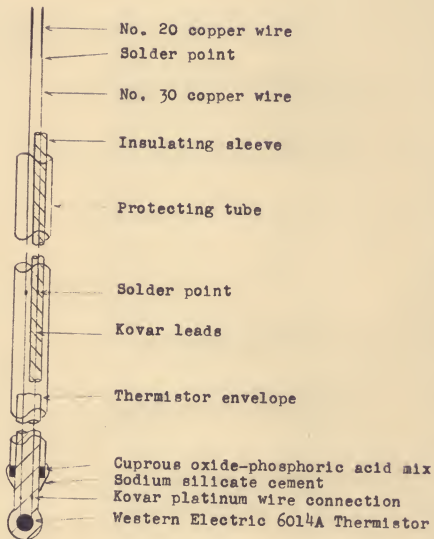
The general form is similar to that of Vold,<sup>19</sup> except for the vacuum top and the tapered joint which is an opposed female onto a male bottom for ease of assembly and cleaning. Although the constructed Dewar did not fit the specifications exactly, it met a submersion test in isopropanol and proved satisfactory in use except for the heater tube (see Figure 3) which could not be used since it was placed at an angle that interfered with the stirrer operation.

### 3. Thermistor and Bridge Assembly.

The thermistor characteristics are described by many writers.<sup>12, 13, 20-22</sup> No details are given in this report, but several points should be borne in mind: First, as a semi-conductor the thermistor is more rugged than other comparable sensing elements; however, it has many limitations and if these limitations are exceeded it may be destroyed. Second, the problem of a thermal time-constant appears to be serious.<sup>20</sup> The time-constant problem may be improperly handled and will be discussed later. "How long does it take to indicate what takes place?" is a good question to ask about any sensing device. It is believed that this factor has not been adequately investigated in many present-day instruments and that the thermistor is comparable to a platinum resistance thermometer

and Mueller Bridge for time sensitivity.

The thermistor was mounted at the end of a thin-walled glass tube (as shown in Figure 5) with  $\text{CuO-H}_3\text{PO}_4$  cement overcoated with waterglass. All attempts to seal to the glass of the imbedded thermistor with appropriate lead glass tubing shorted the lead wires or produced a leaky bottom seal. The Kovar lead wires were soldered to No. 30 B&S copper wires, which were connected to a binding post terminal. To prevent shorting one wire within the tube was covered with the plastic covering stripped from telephone cable. All soldering was done with Ersin three core 45/55 solder. After comparison with a low thermal solder<sup>23</sup> and 50-50 solder, the Ersin showed no apparent potential errors on a 1-cm. square. These potentials were compared on a Leeds and Northrup type K-2 potentiometer. A new non-corrosive solder flux, which in use never failed to provide perfect action, was used. The thermistors, when calibrated, were bound together and placed in an oil bath, in order to compare their respective resistance values under similar conditions. When used in the calorimeter, the thermistor was held by a copper pressure-clip in the thermistor lead tube of the calorimeter top. When the thermistor was placed in position in the calorimeter the stirrer blade was determined to



THERMISTOR ASSEMBLY

Figure 5

pass within 1-mm. of the head in every circumstance.

#### 4. Method of Bridge Construction.

Originally, one watt BTA RMA carbon resistors were used in the Wheatstone bridge but due to some apparent instability and/or drift, they were replaced by 10 and 20 watt wire wound power resistors. These resistors had a much lower drift and were lagged with a  $\frac{1}{2}$ " x 3" iron bolt into a sheet metal holder. Under test there was no apparent change in resistance over 50-150 micro-ampere load, and temperature variation was uniform and much lower than in the case of the carbon resistors. In both cases the resistors were insulated with glass wool and/or Styro-foam to minimize room temperature changes.

The bridge was planned for two methods of construction, each requiring equi-arm techniques, to obtain maximum power. In the first method, which can be called the maximum-unit decade gain, each arm, including the ratio arms, for each decade was to be individually calibrated and inserted in a three-gang, ten position, shorting switch (in Figure 1). In the second method, which can be called the maximum step decade gain, each arm, including the ratio arms for the selected steps, was to be individually calibrated and inserted in a multi-gang, multi-position switch.

The advantage and selection of the second method contrasted to the first, in view of the power limitations of the thermistor, reside in both the method of construction and the convenience of use. In the former, a decade box must be set up, a calibration chart made for each unit and the decade box set each time for measurement. In the latter, a calibration is made requiring a setting for only the steps involved. The power through the thermistor (as in F-I of Figure 1) in any step is never more than a fixed maximum. Since all four arms are equal, the thermistor, being in series with a calibrated decade in the step method (as in A-B-C of Figure 1), consumes only a fraction of the voltage drop in the arm of the Wheatstone bridge.

By limiting the number of personnel and balancing room temperature with a thermostat, a room temperature variation of  $\pm 0.5^{\circ}\text{C}$  could be reduced to  $\pm 0.2^{\circ}\text{C}$  at  $25^{\circ}\text{C}$  over a twenty-four hour period. This was equivalent to  $\pm 20\Omega$  changing to  $\pm 10\Omega$  in the decades of 70,000 $\Omega$  and above. During any one run the temperature did not vary by more than  $\pm 0.1^{\circ}\text{C}$  or  $\pm 5\Omega$  and frequently did not vary this much. Zeroing was done before and after most runs, and an adjusted zero could be made with the CAOR electronic amplifier. In future work resistors with lower temperature coefficients and

impedance effects and the use of a CTB would be necessary to reduce resistance variation. The bridge current was controlled by a 500 K $\Omega$  one watt (see Q in Figure 1) potentiometer in series with five 22.5 volt batteries in parallel. The schematic diagram for the bridge is shown in Figure 1, and is self-explanatory except for the associated circuits described below.

The associated bridge circuit (as shown in Figure 1) except for the thermistor selector switch (O), calibrating switch (S), and meter were eliminated since time and equipment necessary to put all features in operation were not available. It was planned, however, to use a dummy power circuit (D-E-G-H-O-I-N in Figure 1) on both the bridge and non-circuited thermistors in order to avoid abrupt power level changes. Further adjustment resistors in power and bridge components for exact zeros were planned, such as  $R_{4b}$  in Figure 1, in addition to a potential circuit (L-M in Figure 1) for future automatic adjustment of bridge current. The bridge circuit contained a Jones Strip (A-N in Figure 1) to which each component could be tested or attached. This strip acted as a checking and testing point.

The electronic amplifier, now used as a null detector, used originally as a d.c.-recording micro-

voltmeter, is described in a Navy Technical Bulletin.<sup>24</sup> Its characteristics were such that with appropriate voltage on the input bridge almost equivalent sensitivity could be had in the range from  $5 \times 10^5 \Omega$  to  $5 \times 10^2 \Omega$ , to approximately one part in  $10^5$ . Although considerable time was spent in trying to find a pre-amplifying circuit in order to reduce the input noise level to that of the Johnson Noise Limit, no single circuit of suitable impedance range was found. In fact, with the electro-magnetic and/or static noise inside the building, miscellaneous motor and switch noise plus that of input noise, all of which varied non-uniformly, the best level under optimum conditions that could be obtained was of the order equivalent to  $\pm 2$  parts in  $10^5$ .

The indicator circuit consisted of a 60  $\mu$ a panel meter and a 625 NA Triplett Multimeter which was used as a warning guide in order that one could turn the panel meter to its highest sensitivity for final null indication. The Triplett meter could be best used in the voltage ranges, since these ranges affected the amplifier meter the least as a final null indicator (i.e. two parts in  $10^5$ ). Although it was planned to use an automatic timing circuit, the components and circuits were not completed in time for this work.

For further work an automatic device set off of null to allow for time lags of meters or indicators will be necessary, since the rapidity of change is at the limit of human ability to detect the measured null. An off-on setting device was installed to allow the use of three stop watches. These were adjusted to off, reset, and on, to allow for sequential time measurement. The operation of the stop watches was not entirely suitable due to frequent stopping of the watches for unknown reasons.

#### 5. Source or Preparation and Purification of Materials.

With the exception of water and mercury all materials used for this work were purified as indicated below. The mercury was dropped through a one foot tube filled with nitric acid. The mercury was then dropped through three similar tubes filled with water and subsequently vacuum distilled. The distilled water was obtained from War Surplus. This water was prepared by Don Baxter, Inc., Glendale, California, as Item 1491000, Aqua Pro Injections, USP, and was used in the constant-temperature bath without further preparation. The ice used in the constant temperature bath was taken only from those clear sections of commercial cake ice after being washed and chipped. All



other materials except l-limonene were purified by distillation through a Lecky Ewell<sup>25</sup> column of more than 60 theoretical plates at total influx. The column was operated with a total condensation head which had a magnetic takeoff that was operated at 100:1 reflux ratio. The physical constants of the compounds used are as follows:

Material	$n_D^{25}$	Boiling Pt. (20 mm)	Specific Rotation
$\alpha$ -pinene	1.4631	52°C	
$\beta$ -pinene	1.4768	60°C	
<u>d</u> -limonene	1.4702	71°C	+102.66°
<u>l</u> -limonene	1.4710	71°C	ca - 108
<hr/>			
Ethyl benzene	1.4933	(760 mm) 136	

The ethyl benzene was obtained from the Dow Chemical Company, Midland, Michigan. The  $\alpha$ - and  $\beta$ -pinenes were obtained through the courtesy of the Glidden Company, Jacksonville, Florida. The d-limonene was furnished through the courtesy of the Minute Maid Corporation, Plymouth, Florida. The l-limonene was prepared by the pyrolysis of  $\beta$ -pinene, and was kindly supplied by Mr. J. W. Vogh in the Naval Stores Research Laboratory of the Department of Chemistry, University

of Florida.

Although other materials were purified for certain features potentially pertinent to this work, the scope of this investigation eliminated their use.

All materials used calorimetrically in this work were weighed, since the equations used to determine the heat capacities involved masses. Except for mercury, the weighing, to the nearest milligram, of all organic materials was done on a Christian Becker Chainomatic Balance. The mercury was weighed to the nearest hundredth of a gram on a Model AE No. 6036 Metrogram Balance, whose power supply was placed on a Sola (constant voltage) Transformer. A steadily loaded, continually running Metrogram Balance would allow one to detect a  $5 \times 10^{-3}$  gram change during one-half hour quiescent periods.

The para-xylene used as an auxiliary standard consisted of 100 grams of Stock No. 5821, which was purchased from the Paragon Division of the Matheson Company, Inc., East Rutherford, N. J. Due to the limited sample no additional preparation was made. Its  $n_D^{25}$  was 1.4930,

## CHAPTER IV

### EXPERIMENTAL PROCEDURE

#### 1. Amplifier Check and Calibration.

The operation of the amplifier is quite simple. The instrument was left running continuously with a Sola (115-volt) constant voltage transformer and a Stancor (P6145) 117, 105-110-120-volt isolation transformer supplying the operating power. A minimum of twenty-four hours running appears to ensure good operating stability of the amplifier. With the control switch at input short position, the output zero is adjusted at maximum sensitivity. With a balanced bridge or given signal and the amplifier control switch at drift control off, the output is zeroed or set to a desired value. A double throw test signal switch permits testing the amplifier operation under signal. No further calibration was used with null readings, although the instrument could be more exactly calibrated if necessary. A check of the zero or balance of the amplifier output shift can be made with the drift control on and a shorted balanced bridge or a bridge with no power passing through it. By adjustment of the balance potentiometer, the zero of the instrument may be controlled.

## 2. Bridge and Decade Calibration.

The bridge was pre-tested against the Shallcross working decade. The working decades are two Shallcross decades type 733 and 835, which showed good temperature and operating stability. The resistance values of each range of the bridge were found, starting with the highest value, to be:

$$170500 \pm 15\Omega$$

$$119090 \pm 10\Omega$$

$$70490 \pm 9\Omega$$

$$20132 \pm 3\Omega$$

No further overall bridge calibrations were made other than to test the zero for each cumulative decade before and/or after an operation and balancing the final zero on the amplifier control.

Originally an attempt was made to calibrate the decade by parallel shunting methods on a Mueller bridge. Due to galvanometer insensitivity this could not be done, so that each decade up to  $100\Omega$  was (substitutionally) checked against the Mueller bridge versus an NBS standard  $10\Omega$  resistor.

The resistance values of the working decades up to  $100\Omega$  value were compared with a Mueller bridge calibrated against an NBS Standardized  $10\Omega$  Resistor. These values were accurate enough that corrections

were not necessary for this work. A  $1000\Omega$  ohm resistor was constructed from a series of  $100\Omega$  and  $50\Omega$  resistors. This  $1000\Omega$  resistor was calibrated and assembled in units of  $100\Omega$  to have a final measured value of  $1002.934$  (at  $25.00^{\circ}\text{C}$ ). A  $10,000\Omega$  NBS standard resistor was borrowed from the Electrical Engineering Department, University of Florida. The working decade calibration was made against these resistors.

To make a resistance calibration, two additional external decades of  $10^5\Omega$  and 1 to  $10^4$  ohms, connected in series, were used in B-C with Switch S set to 1 as in Figure 1. One lead of each resistor was put respectively to D-E-F and G of Switch O in Figure 1. A lead common to all resistors was inserted into I of Figure 1. Calibration of the decades was made with a 150 micro-ampere total bridge current as set by meter P (Figure 1). These data are shown in Table I for the working decades. In all cases of resistance calibration, the room temperature was  $25.00^{\circ}\text{C} \pm 0.50^{\circ}\text{C}$ , and during a run the variation was usually not greater than  $25.00^{\circ}\text{C} \pm 0.20^{\circ}\text{C}$ . In the bridge, as finally assembled, the resistance step ranges appeared to remain approximately constant, as compared by the amplifier and working decade, to the following values in the step range:

170500  $\pm$  10 ohms

119090  $\pm$  8 ohms

70490  $\pm$  5 ohms

20132  $\pm$  1 ohm

During a period of several weeks no drastic variation was noticed as long as the room temperature did not exceed  $25.00^{\circ}\text{C} \pm 0.50^{\circ}\text{C}$ . Any greater variation was taken as reason for rezeroing operations or waiting for the equalization of room temperature. Also, during this time the balance potentiometer was noticed to be some function of room temperature, which function had been absorbed into the above error. During the latter part of the experimental runs on a second standard, the balance batteries were shorted accidentally. It was noticed, upon the insertion of new batteries, that the bridge zero had apparently shifted to a higher value. This shift was almost twice the value of the original error, added to original step value, but was believed to be within the range of calibration and run errors. For any correction to be made, the correction was applied to the setting value of the working decade for each step value of the bridge decade involved, after adjusting the zero and balance for the lowest valued bridge arm, to the most recently measured or common value.

### 3. Thermistor Calibration.

The thermistors were calibrated by substituting one lead of each thermistor into D-E-F and G of Switch O and a common lead into I, as in Figure 1. The thermistors were bundled into a group and placed in as close contact with the platinum resistance thermometer as possible. All these were inserted as a unit through the cover into the CTB.

When the CTB was filled with mineral oil, the turbo-stirrer and cover were adjusted and a fixed temperature was maintained with two heaters which were controlled by adjustment of the Variacs. One heater, a 250-watt commercial unit, was used to attain a given temperature rapidly. When the temperature of the bath had almost reached the desired range, the heater power was reduced or cut off, and a micro-heater controlled by a Variac was placed in operation.

Although the temperature adjustment depended upon the final temperature desired, control to  $\pm 0.01^{\circ}\text{C}$  was easily reached and maintained for all temperatures above room temperature, as determined by the platinum resistance thermometer. The temperature was more difficult to control at and below room temperature because the apparatus was designed for use at temperatures above  $25^{\circ}\text{C}$  to avoid possible water-vapor condensation.

The CTB was used below 25°C temperature by adding small pieces of dry-ice directly to the bath and reading temperatures on the CTB's thermal leakage heating curve.

The thermistor temperature calibrations were made randomly during heating, quiescent, and cooling periods with all equipment in operation that might be used during a run. Calibration was made for each 5°-interval from and including 15°C through 85°C as compared against the platinum resistance thermometer. One observer read the platinum resistance thermometer while another observer adjusted the balancing decade for the thermistor. Simultaneous readings were made using the platinum resistance thermometer as a base and guide. In most cases above 25°C, when the Mueller bridge was off a precalculated reading by more than  $5 \times 10^{-3} \Omega$ , additional adjustments and readings were made. Generally most readings, except for those below room temperature (25°C) were within  $2 \times 10^{-4} \Omega$  on the Mueller bridge.

In all cases the thermistors led the sensing of any change of temperature before the sensing by the platinum resistance thermometer from one to ten seconds. The setting of the working decade in a step indicated the difference-value of the bridge step value



and thermistor. Differences of 10 $\Omega$  to 40 $\Omega$  could be noticed, as indicated in Table II of this work. Since this random variation could be the sum of noise, thermistor lead or lag, instrument idiosyncrasies, and/or observer error, no special significance was attached to its variation since two observations in the range were generally made for at least one thermistor, and values were most frequently within the range of bridge and resistance calibration.

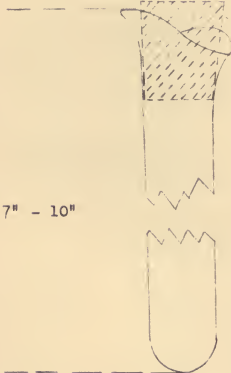
#### 4. Calorimeter Calibration and Run Operation.

The calorimeter calibration and run operations were made in the same manner, the difference being only in the fact that the heat capacity of a standard material in the temperature range for calibration was known.

In the case of mercury the material was weighed by difference directly into the calorimeter and heated prior to the run. For all other organic liquids a tared preheater tube was weighed, filled, heated and weighed again after all heated material had been poured into the calorimeter. The preheater tube (see Figure 6) was kept stoppered with a closely fitted rubber stopper (overlayed with aluminum foil) at all times except during the pouring of liquids into and out of the tube. Either a bath or an electrical heater may be

$\frac{3}{4}" - 1"$ 

Top view



7" - 10"

Rubber stopper  
with or without  
thermometer or  
thermometer well

Side view

PREHEATER TUBE

Figure 6

used to heat the preheater tube. In the present work an electrical heater,<sup>26</sup> which appeared to perform satisfactorily, was used.

The procedure for any run is outlined conveniently as follows:

A. Preliminary Operations

1. The calorimeter stirrer induction motor is started.
2. The filled Dewar or heater tube is weighed.
3. a. The preheater tube is placed in heater and/or tubular heater is placed in Dewar.  
b. The heater is connected to Variac, set to a value which will not cause bumping or bubbling of liquid, and power switch is turned on. (In the case of organic liquids the tubular heater was used also to preheat the Dewar. A bath or electrical heater may be used to heat the tube to approximately the same temperature as the organic liquid in the preheater tube at the same time.)
4. All timing devices are checked for proper sequence operation.
5. The position of calorimeter CTB bracket is checked.

6. CTB is filled with two to three liters of distilled water and chipped clear ice, so that the liquid and ice levels are within three to four inches of the CTB top.
7. Towels, brackets, additional chipped ice and water, and any other necessary material are placed within easy access of support stand.
8. When the preheater tube is within  $10^{\circ}$  of the top limit of heating (in the present procedure  $107^{\circ}\text{C}$ ), a bridge step decade zero is made and recorded on a data sheet. This data sheet is previously prepared with columns for watch time, time seconds, cumulative seconds, decade setting and remarks. If possible decade setting column is filled with values from Table II for the appropriate thermistor.
9. When the temperature of the preheater tube and/or Dewar reaches  $107\text{--}110^{\circ}\text{C}$  the Variac setting is reduced or the power is out off.
10. The Dewar cap and cover are checked as follows:
  - a. Dow-Corning D.C. High Vacuum Grease is spread on all ground glass surfaces or all such surfaces are determined to have

an adequate layer of grease to prevent any leaks.

- b. The thermistor is positioned and any clip or device which is used to hold it in the thermistor tube is adjusted.
- c. Check the clearance between the thermistor and the stirrer (1-mm. is a satisfactory minimum).
- d. Stirrer shaft is lubricated with Silicone grease and stirrer is adjusted so that no binding or excessive protrusion will interfere with capping the Dewar. A small clamp may be used for the adjustment, preferably one that can be left on the shaft during the run.

11. When the temperature of the preheater is 106-107°C a verbal check is made with all observers involved, and arrangement and position of equipment is rechecked visually.

12. When the final check has been made, preparations for the run are completed.

In order for auxiliary observers to know what is happening and record the sequence time for a unit operation, a key word signal is given so they may be ready for any con-

tingency. In this work six key words were used. Upon the word "READY" the auxiliary observer starts the sequence timing and either the pouring operation or the removal of the heater tube from the Dewar filled with mercury was started. Included in this time is the time necessary to recork any empty preheater tubes.

13. Following the key word "NOW", the Dewar calorimeter is capped and placed in the CTB as soon as possible, the time again being rechecked.

14. a. When the Dewar is immersed in the bath, the key word "DEWAR" is called and time is recorded.

b. The CTB cover is inserted over the calorimeter tubes, the bath stirrer inserted and the calorimeter stirrer motor is turned off.

c. The adjustment and clamping of the calorimeter tubes to the top cover of the CTB is made to position the stirrer shaft and motor in best alignment. Small pieces of tape placed on the cover brackets, etc. facilitate this operation.

- d. The stirrer shaft and stirrer motor are connected and a test operation for proper rotation without excessive vibration is made.
15. a. When the foregoing is completed satisfactorily, the final stirring speed is set on the Variac for stirrer motor and the key word "ADJUST" is called and time recorded.
- b. The thermistor leads are connected and the key word "THERMISTOR" is called and time recorded.
  - c. At this time a check is made to see if the thermistor registers a value above or below that set on the working decade. This is done by turning the panel meter to high sensitivity and noting the deflection. If the deflection is not that expected, based upon previous operations, the decade is reset to different values until the proper deflection is found, or the run is stopped.
  - d. From this time on the auxiliary observer sequentially times and records all nulls.
16. a. The CTB stirrer is connected and adjusted as soon as possible; then the key word

- "BATH" is called and the time is recorded.
- b. The level of the ice and water in the top cover CTB is now adjusted to be within one-quarter inch of the top.
  - c. The platinum resistance thermometer is inserted into the CTB and a reading of its resistance value is made as soon and as frequently as is possible, and all times of observation are properly recorded.
  - d. Care must be taken not to interfere with the auxiliary observer during any null reading.
17. During the run, any opportunity for preparation of the next run is made. At the end of the run the disassembly is made in a manner which allows the next run to proceed as soon as possible. The Dewar is drained, cleaned and dried, and it is possible to make as many as two runs every three hours in the range of  $85-15^{\circ}\text{C}$ .

A heat-of-stirring experiment at various stirring speeds was run on 1000 grams of mercury in the calorimeter at room temperature in an empty CTB. The graphical data presented in the next chapter represent the worst and the average conditions at the maximum rate



of stirring used for any run.

The data for a series of runs made by at least three independent auxiliary observers, chosen in random order, are presented in the next chapter of this dissertation. Included with this data are the tabular calculations for the ranges and information mentioned in the Introduction and Theory of this dissertation.

## CHAPTER V

### EXPERIMENTAL RESULTS AND CONCLUSIONS

#### 1. Experimental Data.

General.--In the following sections the data for the experiments, as run, are incorporated into tables in most instances. These data generally represent two or more runs or observations by the writer and auxiliary observers. The data were taken as discussed in Experimental Procedure, but any run was selected randomly. Certain incomplete or partial runs were not incorporated into the tabulated data because of possible confusion in identification. In all cases a time base shift was made so that the starting zero (usually the  $85^{\circ}\text{C}$  point) was approximately the same for all runs. Therefore, in each table the  $85^{\circ}\text{C}$  area was left blank to indicate zero time. This permits the visualization of the differences between runs to be more objective. The tabulated data appear for this reason to be quite similar and permit visual averaging of numbers for use in calculation. As the data were taken the large scale cooling curves ( $T^{\circ}\text{C}$  versus  $t$  seconds cumulative) of this dissertation were plotted. The tabulated data were averaged for use in all possible circumstances.

When the run data on cooling curves showed a dispersion or lack of uniformity a small scale cooling curve plot was made for the time value interpolation. Scarborough's<sup>27</sup> recommendations for significant figures were applied to the computations except possibly at the interpolated values. The interpretation of the curve for interpolation was limited in part by the scale and the estimated location of the curve.

Tabular Calibration and Literature Values.---The tabular resistance and thermistor calibration values were calibrated as given directly or as simple summation values. The values of the resistance temperature calibration data were the working decade setting which represented the difference between the thermistor and the bridge values for the temperature ranges below:

85° through 70°C on the 20K $\Omega$  range

65° through 50°C on the 70K $\Omega$  range

45° through 30°C on the 119K $\Omega$  range

25° through 15°C on the 170K $\Omega$  range

The tables of mercury  $C_p$ , volume weight equivalents, para-xylene and ethyl benzene  $C_p$  are referred to when used in calculations.

The heat-of-stirring experiments indicated that ~~the amount of heat generated per hour under the worst~~ conditions (Figure 8) and at a maximum stirring rate

is approximately

$$1000 \times 0.032 \times \frac{10}{4} \times 1^{\circ}\text{C}^{\star}/\text{hr} = 8 \text{ cal}/^{\circ}/\text{hr}$$

where the starred value is taken to be about a 1000- $\Omega$  change in the thermistor which changes about 4000- $\Omega$ <sup>12</sup> per degree at 25°C. During this part of the experiment the effect of the air conditioner cycle is apparent in the flatter portions of the curve. At approximately 8000 seconds a cloth was placed over the air-filled CTB and Dewar. Figure 8 shows the quieting of the air conditioner cycle and an approximate heating effect, which changes from 8 cal/ $^{\circ}$ /hr to a value considerably less than 1 cal/ $^{\circ}$ /hr.

Caution must be used in the use of any graphs in this dissertation because of the large scale plotted.

The data used for the graphical plots were taken from the a, b and c in each table. The "a" and "b" are used only for the purpose of distinguishing between different runs of the same material, and are used for arbitrary identification.

TABLE I

## RESISTANCE CALIBRATION

Dial Value	Correction	Calibrated Value
100	0.0	100.0
200	- 0.1	199.9
300	- 0.2	299.8
400	0.0	400.0
500	- 0.3	499.7
600	0.0	600.0
700	- 0.4	699.6
800	- 0.7	799.3
900	- 0.5	899.5
1,000	0.0	1,000.0
2,000	+ 1.7	2,001.7
3,000	+ 2.0	3,002.5
4,000	+ 1.7	4,001.7
5,000	+ 2.7	5,002.7
6,000	+ 1.3	6,001.3
7,000	+ 0.9	7,000.9
8,000	+ 1.9	8,001.9
9,000	+ 1.9	9,001.9
10,000	0	10,000
20,000	+ 5	20,005
30,000	- 5	29,995
40,000	0	40,000
50,000	0	50,000
60,000	0	60,000
70,000	- 5	69,995
80,000	+ 2	80,002
90,000	- 3	89,997
100,000	+22	100,022
200,000	0	200,000

TABLE II

## THERMISTOR CALIBRATION

No.	Temperature		Platinum Resistance Thermometer in Ohms on Mueller Bridge			Arm Difference for Thermistor Resistance Value			
	$^{\circ}\text{C}$	$^{\circ}\text{K}$	$R_0$	A + Bx10 <sup>3</sup>	$R_{\Sigma}$	No. 1	No. 2	No. 3	No. 4
1	15.00	288.16	25.4790	1.5263	27.0081 27.0277 27.0356 27.0399	9073	14243	2265	3140
2	20.00	293.16	25.4790	1.9921	27.4712 27.4715 27.4710 27.4712	42143	44642	44860	44442
3	25.00	298.16	25.4790	2.5335	28.0141 28.0156 28.0163 28.0172	70830	73106	64263	64952
4	30.00	303.16	25.4790	3.0405	28.5199 28.5200 28.5205 28.5207	39907	41922	34454	35121
5	35.00	308.16	25.4790	3.5472	29.0268 29.0269 29.0270 29.0267	55874	57616	51376	51980

<sup>a</sup>Interpolated value

TABLE II - Continued

No.	Temperature		Platinum Resistance Thermometer in Ohms on Mueller Bridge			Arm Difference for Thermistor Resistance Value			
	°C	°K	R <sub>0</sub>	A + Bx10 <sup>3</sup>	R <sub>Σ</sub>	No. 1	No. 2	No. 3	No. 4
6	40.00	313.16	25.4790	4.0540	29.5339	68401	69820	64592	65146
7	45.00	318.16	25.4790	4.5609	30.0409	78065	79373	79484	75480
8	50.00	323.16	25.4790	5.0675	30.5509	37178.0	38312.0	34620.0	34186.4
9	55.00	328.16	25.4790	5.5742	31.0550	43256.2	44236.2	41118.2	41625.0
10	60.00	333.16	25.4790	6.0810	31.5811	48295.0	49140.2	46512.0	46888.0
11	65.00	338.16	25.4790	6.5875	32.0690	52052.0	52791.0	50527.5	50826.0
12	70.00	343.16	25.4790	7.0942	32.5761	4864.5	5502.5	3585.0	3885.5
13	75.00	348.16	25.4790	7.0601	33.0831	7420.0	7974.4	6324.0	6599.5
14	80.00	353.16	25.4790	8.1076	33.5903	9504.0	9981.7	8577.0	8809.6
15	85.00	358.16	25.4790	476 <sup>a</sup>	34.0092 <sup>b</sup>	1122.9	11634.0	10430.3	10634.4

<sup>a</sup>Interpolated value<sup>b</sup>Approximated by visual interpolation

TABLE III  
 INTERPOLATION TABLE FOR  
 THE HEAT CAPACITY OF MERCURY  
 From 100°C to 0°C<sup>26</sup>

T°C	C <sub>p</sub> gm	C <sub>p</sub> mole	Δ <sub>1</sub> mole	Δ <sub>2</sub> mole	Δ <sub>3</sub> mole
0		6.6972			
20	0.03332	6.6683	0.0289	0.0025	
	0.03327	(6.6564) <sup>a</sup>	0.0264		0.0004
40	0.03319	6.6419		0.0021	
	0.03314	(6.6308) <sup>a</sup>	0.0243		0.0004
60	0.03307	6.6176		0.0017	
	0.03302	(6.6076) <sup>a</sup>	0.0226		0.0004
80	0.03296	6.5954		0.0013	
			0.0213		
100		6.5741			

<sup>a</sup> Interpolated value



TABLE IVa

Computed  $C_p$  Values of Ethyl Benzene<sup>32</sup>

$T^{\circ}\text{C}$	$C_p/\text{gm-cal}$
20 . . . . .	0.4150 <sup>x</sup>
30 . . . . .	0.4222 <sup>x</sup>
40 . . . . .	0.4294
50 . . . . .	0.4367
60 . . . . .	0.4440
70 . . . . .	0.4512
80 . . . . .	0.4583

TABLE IVb

Para-Xylene  $C_p$  Values<sup>32</sup>

$T^{\circ}\text{C}$	$C_p/\text{gm-cal}$
0 . . . . .	0.4013
20 . . . . .	0.4057
40 . . . . .	0.4198
60 . . . . .	0.4350
80 . . . . .	0.4513
100 . . . . .	0.4686

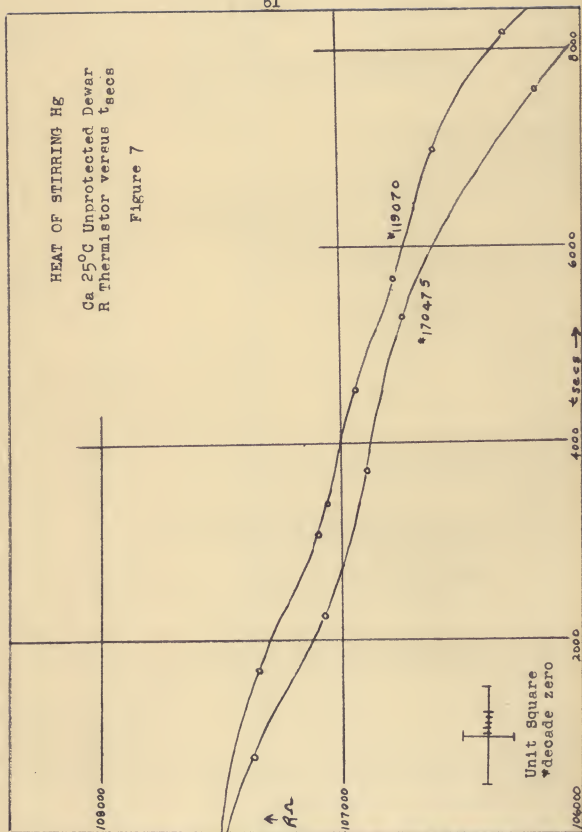
 $C_p$  in calories

<sup>x</sup> These values interpolated; all others extrapolated.

## HEAT OF STIRRING HG

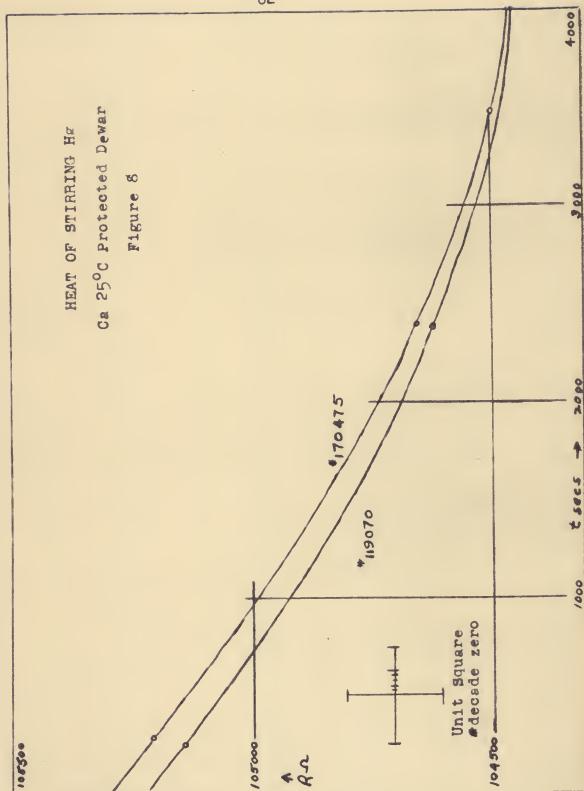
Ca 25°C Unprotected Dewar  
R Thermistor versus t secs

Figure 7



HEAT OF STIRRING  $H\sigma$   
Ca 25°C Protected Dewar

Figure 8



Calibration Runs with Mercury and Ethyl Benzene.--

The run numbers were assigned arbitrarily for identification between runs. These run numbers were transformed to a, b and c, respectively, for tabular use. In all tables the  $T^{\circ}\text{C}_*$  refers to the above transformation and each temperature may be identified with a decade setting for a particular thermistor in Table II.

In Tables V through XII the columnar numbers serve to cross-identify the mathematical operations except for (1) which is identified with  $T^{\circ}\text{C}$ .

In all equations, their transformations and resultant computations, the following systematic notation was used. The time values were always selected for a  $10^{\circ}\text{C}$  interval. This was determined by taking the averaged or smoothed values opposite to that of the temperature selected and adding this value to the averaged or smoothed values of the next lower  $5^{\circ}\text{C}$  value. All tabular computations are carried on the line of the selected temperature value. Except for Tables V through VII the  $C_p$  of the calorimeter  $C_0$  is 3.9 calories/gram/ $^{\circ}$ . In all equation forms  $\Delta t$  of Equation VIII is replaced by  $t$ , the  $\Delta$  being understood. Numbered subscripts replace the lettered subscripts of Equation VIII, the 1 subscript referring

TABLE V

DATA FOR

## MERCURY CALIBRATION OF CALORIMETER

°C	Run Number				
	1000 grams			500 grams	
	3-1	3-3	9-1	10-1	10-2
85	0	0	0	0	0
80	131.8	131.4	128.4	116.0	116.6
75	261.6	269.4	265.6	239.4	238.8
70	406.8	416.8	411.6	370.4	367.8
65	566.0	577.6	570.6	510.2	507.8
60	732.2	743.8	735.2	651.4	651.4
55	925.7	938.1	930.0	815.0	821.8
50	1132.3	1142.6	1134.6	991.8	1001.8
45	1241.1	1373.0	1242.6	1085.2	1097.0
40	1623.3	1631.5	1622.4	1405.2	1430.8
35	1852.1	2035.4	1855.4	1653.2	1687.0
30	2193.5	2262.7	2198.0	2198.0	1989.6
25	2588.7	2607.7	2593.8	2297.2	2329.0
20	2942.5	3143.3	2948.8	2597.6	2636.2
15	3673.5	3710.5	3707.4	3242.4	3283.0

at all times to 1000 grams of mercury. The 2 subscript refers to the second standard or unknown substance as may be required. In the tabular equation each table operation is identified with the equation used. All tabular  $C_p$ 's are referred and substituted with the appropriate table number, the correct temperature being that of the temperature used.

The rearranged Equation VIII used for Table VI

18

Equation	Tabular Columns
$C_0 = C_1 \left( \frac{t_2^{m1} - t_1^{m2}}{t_1 - t_2} \right)$	$= III \frac{(5) - (6)}{(2) - (3)} = III \frac{(7)}{(3)}$

where the 2 subscript is for 500.00 grams of mercury. The average value of 10.06 calories/gram/ $^{\circ}$  was expected since the inner section weighed about 50.0 grams before assembly. The mean deviational sigma of 2/1200 appears to indicate that the values used were of statistical significance. The bump in the cooling curve appeared in all later runs and will be discussed in the Summary of this chapter.

The rearranged Equation VIII used for Table VII

18

Equation	Tabular Columns
$C_0 = \frac{t_2^{m1}c_1 - t_1^{m2}c_2}{t_1 - t_2}$	$= \frac{(4)III - (5)Va}{(2) - (3)} = \frac{(6)}{(7)}$

TABLE VI

MERCURY CALIBRATION AND TABULAR  $C_0$ 

$T^{\circ}C^{**}$ (1)	$t_1$ (2)	-	$t_2$ (3)	=	$\Delta t$ (4)	$t_2 m_1$ (5)	-	$t_1 m_2$ (6)	=	$\Delta t m$ (7)	$C_0^{**}$ (8)
85	a.										
	b.										
	c.										
80	a	131.8	116.0	26.7	23910	13220	10680	13.18			
	b	131.4	116.6								
	c	128.4									
75	a	129.8	123.4								
	b	138.0	122.2								
	c	137.2									
70	a	145.2	131.0	46.4	26990	15810	11170	7.95			
	b	147.4	129.0								
	c	146.0									
65	a	159.2	139.8								
	b	160.8	140.0								
	c	159.0									
60	a	166.2	141.2	66.0	31100	18870	12230	6.13			
	b	166.2	143.6								
	c	164.6									
55	a	193.5	163.6								
	b	194.3	170.4								
	c	194.8									
50	a	206.6	176.8	63.0	37000	21650	15400	8.10			
	b	204.5	180.0								
	c	204.6									
45	a	108.8	93.4								
	b	230.4	95.2								
	c	108.0									
40	a	382.2	320.0	40.0	48000	26000	22000	18.26			
	b	258.5	338.8								
	c	379.8									
35	a	298.8	248.0								
	b	165.8	256.2								
	c	233.0									
30	a	341.3	545.0	77.0	57600	32650	24950	10.78			
	b	227.3	297.6								
	c	342.6									
25	a	395.2	79.2								
	b	345.0	344.4								
	c	395.4									
20	a	353.8	300.4	207.0	95300	58000	37300	6.00			
	b	535.6	307.2								
	c	355.4									
15	a	851.0	644.8								
	b	567.2	652.8								
	c	758.6									

\* See Pages 53, 55 and 65

\*\* See Page 65

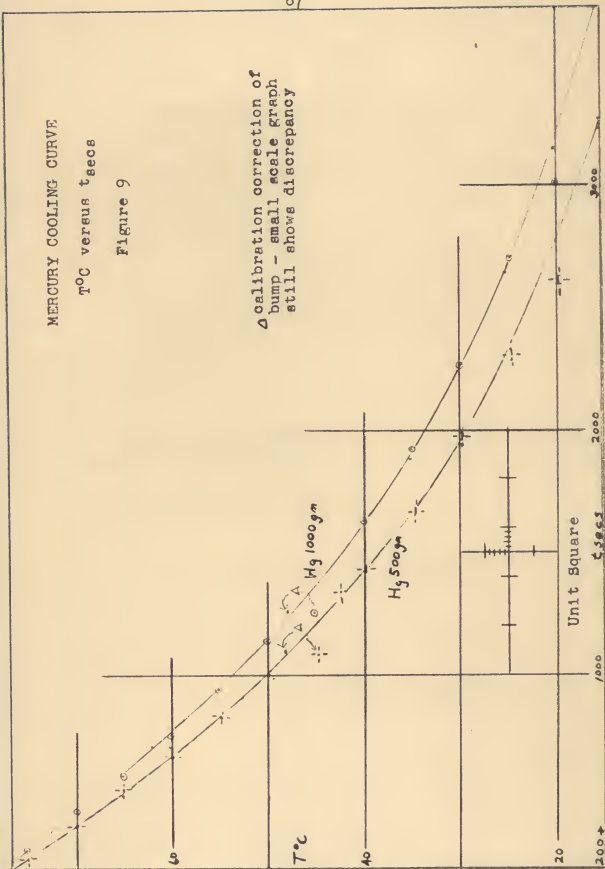
Values in (5), (6) and (7) x  $10^{-1}$

# MERCURY COOLING CURVE

$T^{\circ}\text{C}$  versus  $t_{\text{sec}}$

Figure 9

$\Delta$  calibration correction of  
bump - small scale graph  
still shows discrepancy





where the 2 subscript is for 65.34 grams of ethyl benzene. The cooling curve for ethyl benzene is most similar to that for 500.0 grams of mercury. The tabular  $C_p$ , using ethyl benzene as a secondary standard, is approximately 0.40 the averaged value determined for mercury. A rounded calorimeter  $C_p$  value of 10.0 cal/gram/ $^{\circ}$  was used for the test liquids ethyl benzene and para-xylene. For the terpenes a calorimeter  $C_p$  value of 3.9 cal/gram/ $^{\circ}$  was used following the technique of Spear.<sup>11</sup> This might indicate that the apparent or effective  $C_p$  of the calorimeter is less than the actual  $C_p$  due to thermistor characteristics, stirring problems or heat transfer coefficients, which will be discussed further in the Summary.

In Table VIII the  $C_p$  for ethyl benzene and para-xylene are computed from Equation VIII, rearranged as follows:

$$C_p = C_2 = \frac{(t_2 - t_1)C_0 + t_2 m_1 C_1}{t_1 m_2} = \frac{((2) - (3))C_0 + (3)m_1 III}{(2)m_2} = \frac{(6) + (7)}{(9)}$$

where  $m_1$  and  $C_0$  are defined (see page 65) and  $m_2$  is for "a" 65.34 grams of ethyl benzene and "b" for 64.18 grams of para-xylene

The data in Tables VII and VIII have been smoothed from small scale plots in order to allow a more useful comparison. The smooth computed  $C_p$  data for the test

standards vary from less than two to thirteen percent, in the range from 80°C to 20°C respectively.

The averaged computed value for ethyl benzene of 0.459 is 1.022 larger than the average literature value of 0.449. For para-xylene a similar comparison reveals that 0.466 is 1.093 larger than the average literature value of 0.426.

These values are not entirely satisfactory due to data dispersion, errors in rounding and a possible error in smoothing. The inter-comparison of smoothing formulas and methods could appear to be of little value if dispersion alone is too great. For this reason the subsequent data will not be smoothed in this work. Features which may affect these data will be discussed in the Summary of this Chapter.

TABLE VII  
ETHYL BENZENE CALIBRATION AND  
TABULAR CALCULATION OF  $C_o$

$T^{\circ}C$ (1)	$t_1^M$ (2)	$t_2^M$ (3)	$\Delta t$ (4)	$t_2^M c_1$ (5)	$t_1^M c_2$ (6)	$= \Delta t m$ (7)	$C_o$ (8)
80	267	238	29	7818	8000	a	a
60	357	314	43	10380	10365	15	0.4
40	537	465	72	15380	15080	300	4.2
20	1093	913	180	30443	29660	783	4.4

<sup>M</sup> See pages 53, 68 and 69.  
a Anomalous, see page 69.

TABLE VIII  
 TABULAR CALCULATED VALUES OF  $C_p$  FOR ETHYL BENZENE AND  
 PARA-XYLENE USING MERCURY AS STANDARD

$T^{\circ}C$	c	$t_1$	$t_2$	$\Delta t$	$C_o \Delta t + t_2 C_{p1}$	$\Sigma$	$t_{1m2}$	$C_p$
(1)	(2)	(3)	(4)	(5)	(6)	(8)	(9)	(10)
80	a	267	238	29	290	8108	17400	0.464
	b	267	233	34	340	8025	17130	0.468
60	a	357	314	43	430	10810	23390	0.462
	b	357	307	50	500	10690	22910	0.466
40	a	537	465	72	720	16080	35200	0.457
	b	537	455	82	820	15920	34460	0.462
20	a	1093	913	180	1800	32243	71450	0.454
	b	1093	912	181	1810	32149	70150	0.458

\* See pages 53, 68 and 69.

c Compare  $C_p$  a with Table IVa - Ethyl. Benzene  
 b with Table IVb - Para-Xylene

ETHYL BENZENE ©

and

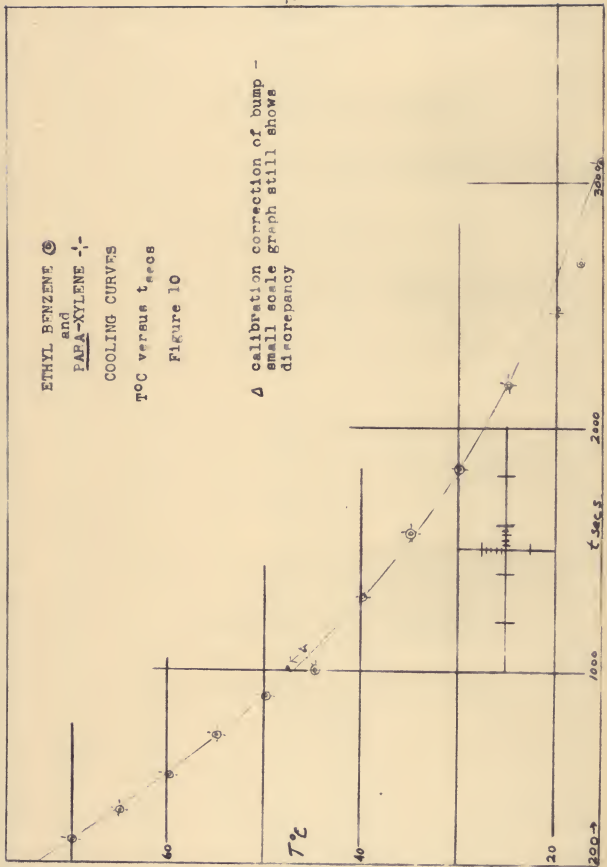
PAPA-XYLENE -1-

COOLING CURVES

T°C versus  $t_{sec}$

Figure 10

Δ calibration correction of bump -  
small scale graph still shows  
discrepancy



The Approximate  $C_p$  of the Terpene Hydrocarbons.—

The tabular calculated  $C_p$ 's of  $\beta$ -pinene and d-, l-limonenes and  $\Delta$ -pinene are given in Tables IX, X, XI and XII, respectively. Again the cooling curves of the above substances, respectively Figures 11, 12, 13 and 14, are similar to mercury and ethyl benzene with the same bump in the usual 45°C location.

The rearranged Equation VIII used for the following data is

Equation	Tabular Columns
$C_p = C_2 = \frac{(t_1 - t_2)C_0 + t_2 c_1 m_1}{t_1 m_2} = \frac{((2) - (3))C_0 + (3)III m_1}{(2)m_2} = \frac{(4)C_0 + (5)}{(6)} = \frac{(8)}{(6)}$	

where  $C_0$  and  $m_1$  are defined (see page 65) and  $m_2$  is as follows:

<u>Table No.</u>	<u>Substance</u>	<u>Mass in grams</u>
IX	$\beta$ -pinene	64.88
X	<u>d</u> -limonene	62.70
XI	<u>l</u> -limonene	55.13
XII	$\Delta$ -pinene	64.03

A  $C_p$  literature survey showed only a limonene sample<sup>31</sup> of unknown purity to have a known value of 0.438 at 20°C. If it is a natural product and of the d configuration the value from Table X, at 20°C of 0.422, is

$$\frac{0.438 - 0.422}{0.438} \times 100 = 3.66\%$$

The values of all the terpenes used except the l-limonene, which was a pyrolysate, appear very similar at 20°C. In view of the previous data it appears that all values are of the correct order, but not of great accuracy. Since any further discussion of the results and computed values should be considered in a more complete scope, this will be covered in the following Summary.

TABLE IX

TABULAR CALCULATED VALUES OF  $C_p$  FOR  $\beta$ -PINENE  
VERSUS MERCURY STANDARD

$T^{\circ}\text{C}$	$t_1^* - t_2 =$	$\Delta t$	$t_{201m1}$	$t_{1m2}$	$\Delta t_{co} = B$	$\Sigma$	$C_p$	
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
85 a								
b								
80 a	111.2	- 32.9	7666	17260	-128.3	7538	0.437	
b	113.0							
75 a	120.0							
b	120.9							
70 a	127.8	- 50.5	8786	20541	-197.0	8589	0.418	
b	130.2							
65 a	134.0							
b	140.1							
60 a	142.4	- 63.2	10352	24440	-246.5	10106	0.414	
b	144.2							
55 a	169.0							
b	171.4							
50 a	178.0	- 48.0	12758	28093	-187.2	12571	0.448	
b	178.8							
45 a	92.6							
b	94.8							
40 a	327.8	- 39.0	19283	33738	-152.1	19131	0.567	
b	330.1							
35 a	253.8							
b	254.7							
30 a	289.6	- 61.0	19695	42556	-237.9	19457	0.457	
b	294.4							
25 a	337.0							
b	340.7							
20 a	299.8	-175.6	32800	75262	-684.8	32115	0.428	
b	301.5							
15 a	632.6							
b	638.2							

\* See Table V and/or VI

a See pages 53 and 55

b See pages 53 and 55



# $\beta$ -PINENE COOLING CURVE

$T^{\circ}\text{C}$  versus  $t_{\text{secs}}$

Figure 11

4 calibration correction of  
bump - small scale graph  
still shows discrepancy

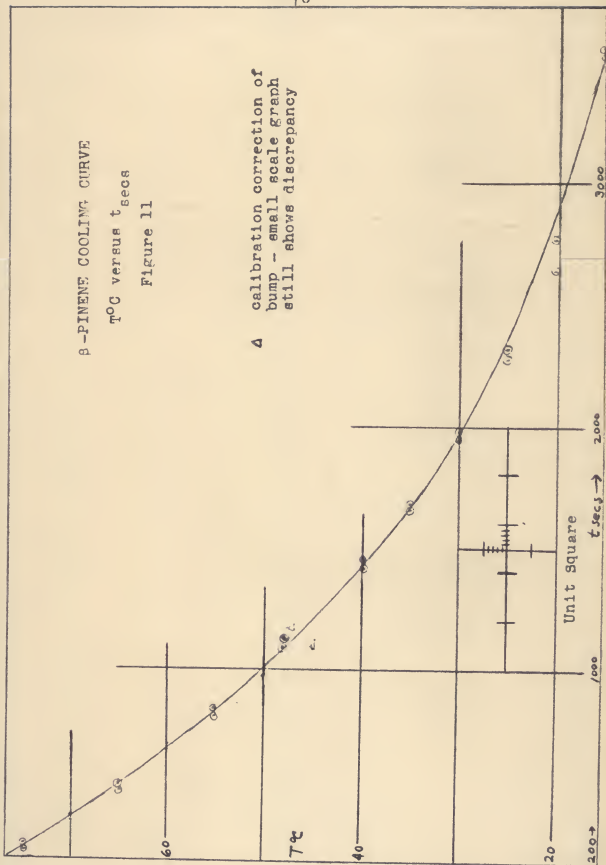


TABLE X

TABULAR CALCULATED VALUES OF  $C_p$  FOR d-LIMONENE  
VERSUS MERCURY STANDARD

T <sup>o</sup> C	$t_1$	$t_2$	$\Delta t$	$t_{2m1}c_1$	$t_{1m2}$	$\Delta t_{co}$	$\Sigma$	$C_p$
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
85	a							
	b							
	c							
80	a	131.1	- 13.9	8383	16645	- 54.2	8329	0.500
	b	119.4						
	c	135.4						
75	a	121.8	- 25.7					
	b	125.6						
	c	121.6						
70	a	132.1	- 41.4	9087	19849	-161.5	8925	0.458
	b	132.8						
	c	129.6						
65	a	145.5	- 41.9					
	b	144.6						
	c	141.0						
60	a	144.1	- 57.7	10562	23617	-225.0	10337	0.434
	b	147.4						
	c	147.0						
55	a	172.7	- 57.8					
	b	174.5						
	c	172.4						
50	a	182.9	- 27.4	12778	27147	-106.9	12671	0.467
	b	184.0						
	c	180.8						
45	a	203.0	- 20.6					
	b	96.4						
	c	96.2						
40	a	227.4	- 34.8	16103	30153	-135.7	15968	0.530
	b	337.8						
	c	330.6						
35	a	354.2	- 33.9					
	b	259.8						
	c	255.8						
30	a	200.0	- 10.0	21419	40943	- 39.0	21380	0.522
	b	300.5						
	c	296.0						
25	a	349.4	-215.9					
	b	344.3						
	c	342.8						
20	a	466.8	-213.4	31540	72727	-832.3	30708	0.422
	b	300.6						
	c	302.8						
15	a	485.8	-113.5					
	b	645.3						
	c	643.6						

\* See Table V and/or VI

a,b,c See pages 53 and 55

# d-LIMONENE COOLING CURVE

$T^{\circ}C$  versus  $t_{secs}$

Figure 12

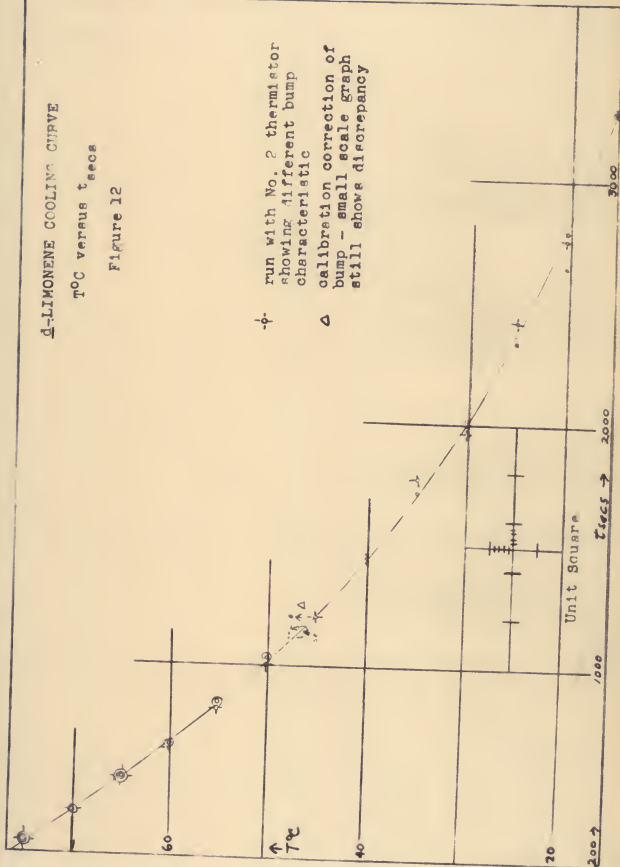


TABLE XI

TABULAR CALCULATED VALUES OF  $C_p$  FOR 1-LIMONENE  
VERSUS MERCURY STANDARD

$T^{\circ}C$	$t_1^* - t_2 = \Delta t$	$t_2 m_1 c_1 - t_1 m_2 = \Delta t_{co}$	$\Sigma$	$C_p$			
(1)	(2) (3) (4)	(5) (6) (7)	(8)	(9)			
85 a							
b							
80 a	121.2	- 17.5	8174	14637	- 68.3	8105	0.554
b	119.4						
75 a	127.8						
b	127.6						
70 a	136.6	- 32.9	9367	17455	-128.3	9239	0.529
b	136.4						
65 a	147.7						
b	146.8						
60 a	150.5	- 47.9	10873	20768	-186.8	10686	0.514
b	151.2						
55 a	177.8						
b	178.2						
50 a	186.4	- 32.3	13279	23872	-125.9	13153	0.551
b	185.0						
45 a	98.0						
b	98.0						
40 a	241.4	- 37.0	16031	28669	-144.0	15887	0.554
b	340.4						
35 a	261.4						
b	263.0						
30 a	300.1	- 19.3	21417	36000	-106.4	21316	0.592
b	300.4						
25 a	348.0						
b	348.6						
20 a	307.5	-203.9	35189	63950	-795.0	34394	0.538
b	305.0						
15 a	649.5						
b	650.0						

\* See Table V and/or VI

a See pages 53 and 55

b See pages 53 and 55

## 1-LIMONENE COOLING CURVE

 $T^{\circ}\text{C}$  versus  $t_{\text{secs}}$ 

Figure 13

- + run showing effect of interrupted stirring  
 Δ calibration correction of bump - small scale graph still shows discrepancy

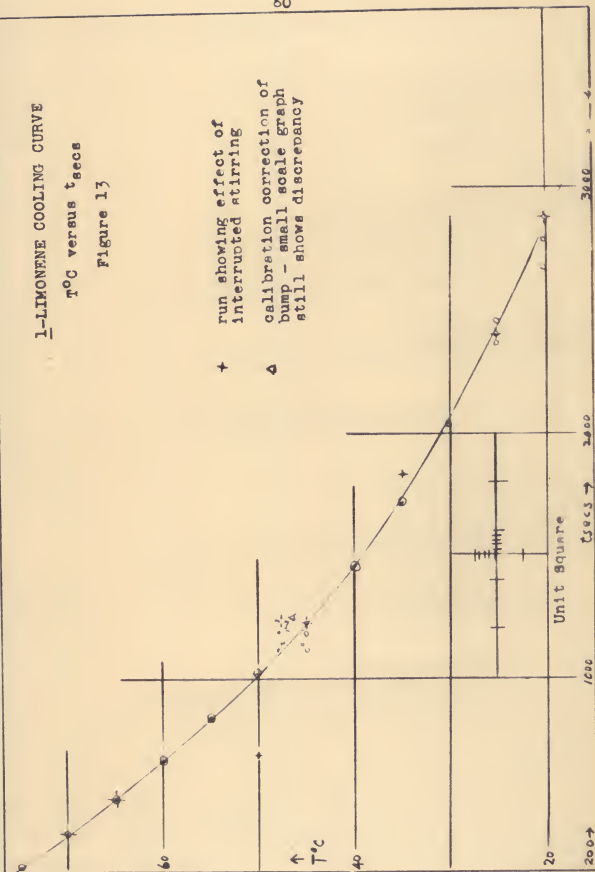


TABLE XII

TABULAR CALCULATED VALUES OF  $C_p$  FOR  $\beta$ -PINENE  
VERSUS MERCURY STANDARD

$T^{\circ}C$	$t_1^*$	$-t_2$	$= \Delta t$	$t_2 m_1 c_1 -$	$t_1 m_2 = \Delta t_{co}$	$\Sigma$	$C_p$	
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
85 a		81.5						
b								
80 a		116.4	- 49.6	7116	16999	-193.4	6922	0.408
b								
75 a		123.3						
b		179.1						
70 a		132.5	- 43.5	9017	20271	-169.7	8848	0.436
b		179.1						
65 a		143.0						
b		148.5						
60 a		147.5	- 54.3	10661	24120	-211.8	10450	0.433
b		151.3						
55 a		174.8						
b		179.2						
50 a		183.7	- 52.3	12616	27724	-204.0	12412	0.448
b		184.1						
45 a		208.0						
b		101.2						
40 a		229.8	- 49.3	17258	33295	-192.3	17066	0.512
b		644.1						
35 a		350.7						
b		267.6						
30 a		201.1	-134.0	19313	41811	-523.0	18790	0.449
b		309.5						
25 a		351.6						
b		358.6						
20 a		466.8	-217.0	31411	74275	-846.3	30565	0.412
b		319.2						
15 a		496.9						
b		687.4						

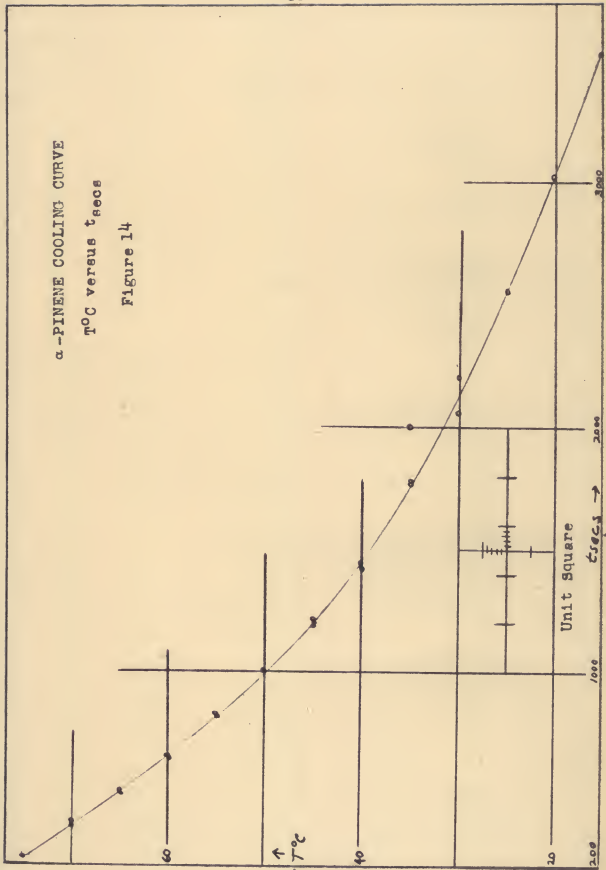
\* See Table V and/or VI

a See pages 53 and 55

b See pages 53 and 55

$\alpha$ -PINENE COOLING CURVE $T^{\circ}\text{C}$  versus  $t_{\text{secs}}$ 

Figure 14



## 2. Discussion, Summary and Conclusions.

A thermally-sensitive resistance (thermistor) has been incorporated into a moderately wide range step-unit Wheatstone bridge. By using a well designed DC amplifying micro-voltmeter to detect the bridge null, as a micro-ammeter, and by using a static temperature calibration technique, at uniform increments, the thermal transients of dynamic systems have been measured at a rapid rate of temperature change. These measurements were made using commercial components throughout, without any special testing of the time these assembled components require to show a given signal or change of signal. When this sensing and indicating device is used in a thermally lagged (Dewar) system, kept in adequate thermal agitation and contact, the thermistor appears to register the temperature of the system correctly but with certain characteristics, which do not appear to have been reported previously as found in this investigation.

The positive features of this investigation are several and varied in their interrelationships.

First, the heat capacity data are quite dispersed and are in poor to fair agreement with the literature values for ethyl benzene (27 percent variant), para-xylene (5.0 percent variant) and d-limonene (3.6 per-



cent variant). These  $C_p$  values appear to be of the right order and approximate magnitude. The results do not appear to be uniformly variant among values or between substance-class according to the computed data. The hyperbolic cooling curves of Figures 9-14 should yield straight lines when transformed to a  $\log T^\circ\text{C}$  versus  $t$  seconds plot as in Figure 15 for ethyl benzene and mercury. The straight line is used as a test-proof for a system obeying Newton's law of cooling, which can be derived from Equation VII in the form

$$\frac{dT}{dt} = A''\Delta T = A''T_1 - T_2 = -A''T_2 \quad (\text{XXIII})$$

when  $T_1 \approx 0$ . Rearranging and integrating we obtain

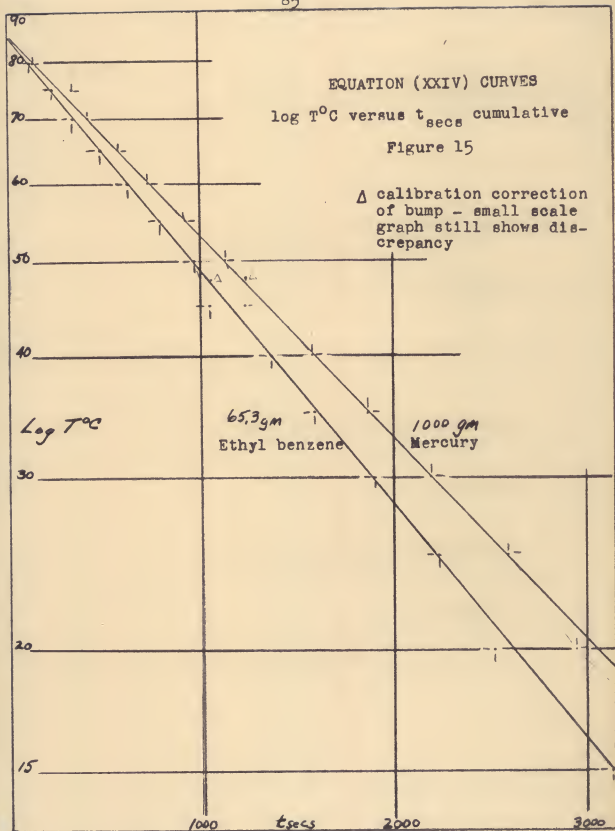
$$\log T_2 = -A''t + C \quad (\text{XXIV})$$

where  $C$  is an arbitrary integration constant, and the negative sign indicates a temperature decrease.

Since this handling of logarithms is not convenient with graphs or an electrical computer, advantage was taken of the equi-spaced points. This alternative test from Equation XXIII when the  $dT$  units are equal, i.e.  $10^\circ$

$$\text{is } \frac{10}{dt} = A''T_2 \text{ or } \frac{1}{dt} = \frac{A''}{10} T_2 = A''' T_2 \approx \frac{1}{\Delta t} \quad (\text{XXV})$$

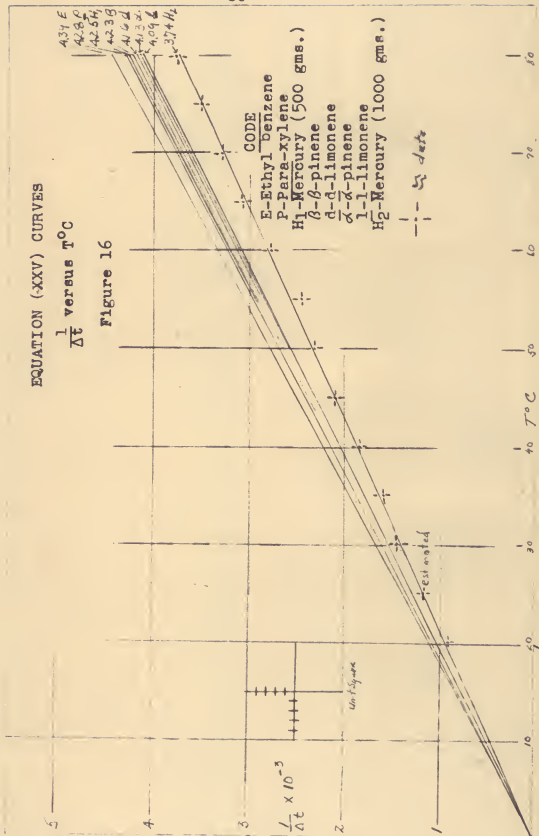
The averaged data from the various runs were plotted on a small scale graph using the Equation XXV for the



## EQUATION (XXV) CURVES

 $\frac{1}{\Delta t}$  versus  $T^{\circ}\text{C}$ 

Figure 16



coordinate selection. Figure 16 shows the data on a large scale plotted by slope line transfer which was used because the exact points on the graph would be obliterated by the lines drawn. Each plotted line depends upon the interpretation of the original data, but represents the best line that can be drawn through the individual points or their visual mean. The points for ethyl benzene, para-xylene and l-limonene were more dispersed than the other substances used. An attempt to run the smooth curve data from Figure 16 back to the  $C_p$  data improved the values of any one run per se, but did not necessarily improve the overall or absolute accuracy. Additionally, this attempt showed that no simple resolution of the  $C_p$  of standard materials between themselves could be made with the data and plots used.

Second, Figures 15 and 16 show reasonable agreement with Newton's law of cooling within the limitations of the devices used for measurement. The fact is that several of these lines (in Figure 16) offer sufficient experimental evidence which appears to contradict the impression of many textbooks on calorimetry<sup>1-2</sup> and heat<sup>5-7</sup> that Newton's law of cooling is more closely connected with radiation than conduction.

The total immersion Dewar used in this investigation was designed and constructed with the intention

of keeping radiation effects small to negligible. Any convection process connected with this investigation is believed to be primarily a function of thermal conduction because of the high stirring rate. These considerations leave conduction as the most important method by which heat can be transferred from the Dewar.

It is difficult to believe that Newton, using a thermometer which indicated temperature by rarefactions<sup>9</sup> of oil, could necessarily see the small variations of a heat function that varies with temperature, as is indicated by the differences in the slopes of all curves. This difficulty is enhanced by the lack of constant temperature of the strong draught of air he might have had available. Figure 16 supports Newton's observations, and offers a concise method for the smoothing and analysing of data. Each line of Figure 16 passes through  $0^{\circ}\text{C}$ , the CTB temperature at  $1/\Delta t \approx 0$ , for all substances used.

If the substances measured have constant or linear functions of  $C_p$ , the effect of this  $C_p$  variation will be summative and will appear as a change of slope, whose variations cannot be simply interpreted at present. The reason for this is that the properties of the system and the measuring device appear to have certain characteristics (as discussed later) which need further investi-

gation and/or delineation. With improvement of the method and measuring devices, this technique appears to be one of many possible for the evaluation of the  $f(T)$  function previously intimated.

Third, the limitation upon the range of Newton's law of cooling by the same texts<sup>5-7</sup> and others<sup>1-2</sup> does not appear to be uniform in application. From these data, dispersed as they are, the potential wider range confirms and extends even that of Spear<sup>11</sup> by a moderate amount. The general impression of multiplicity and conflict with regard to all phases of heat capacity determinations are adequately delineated by Partington.<sup>33</sup>

Fourth, the use of a static calibration technique for a dynamic temperature measurement raises the question of the validity of comparison for a negligible rate of change against two or more co-existent high rates of change. There may be some high rate of change systems that need the foregoing problem solved, when this method is further correlated and improved. It appears that this method and technique may help to solve such a problem, and possibly answer many other questions about dynamic systems.

Fifth, although the so-called "bump" in the cooling curve may have appeared in the literature under some other consideration,<sup>12-14, 20-22</sup> it does not seem to have

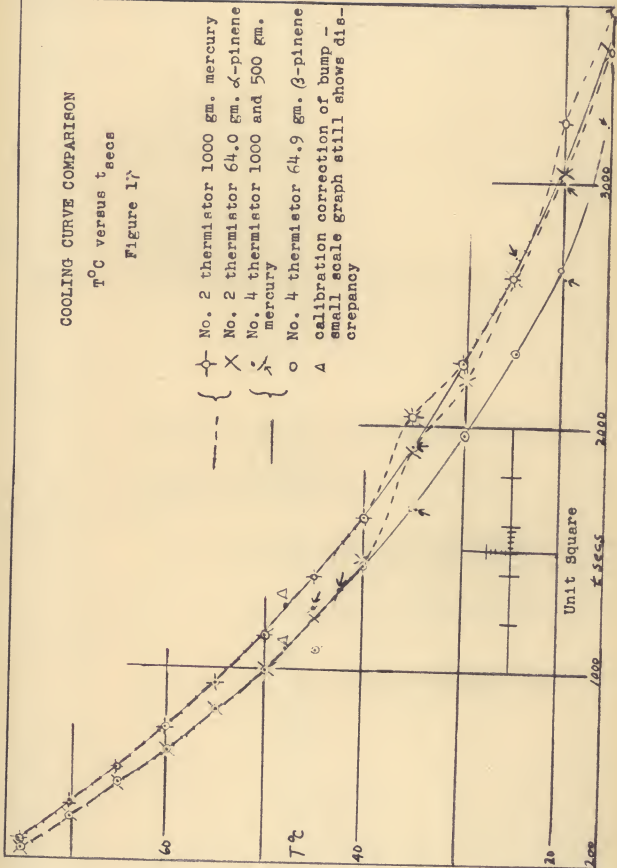
been reported explicitly as has been observed in this investigation. This seeming bump appeared to shift upon recalibration in magnitude and direction, which is roughly shown by the  $\Delta$  in Figures 9-17. During recalibration the values around the bump area appeared to shift the most. There was approximately 1000 $\Omega$  change near 50°C for all thermistors compared to a 30-100 $\Omega$  change at other temperatures during the month of use. The use of a power level of 14-28 micro-watts is less than reported in other recent investigations and not believed excessive. In the area of the bump the rate of travel of the meter needle appeared to change. With the instrumentation available further investigations of these properties were not possible. Additionally, the power preloading of thermistors seems to be most desirable, since calibration discrepancies cannot be solely attributed to aging. If there are unstable areas of use, the critical selection of semi-conductors might appear to be necessary under dynamic conditions. The thermistors used in this investigation had another characteristic, other than the bump (see page 29 of this report), that hindered their calibration and use. Consideration of curve displacements for Figures 16 and 17

# COOLING CURVE COMPARISON

$T^{\circ}\text{C}$  versus  $t_{\text{secs}}$

Figure 1'

- $\circ$  No. 2 thermistor 1000 gm. mercury
- $\times$  No. 2 thermistor 64.0 gm.  $\alpha$ -pinene
- $\Delta$  No. 4 thermistor 1000 and 500 gm. mercury
- $\circ$  No. 4 thermistor 64.9 gm.  $\beta$ -pinene
- $\Delta$  calibration correction of bump - small scale graph still shows discrepancy





are not explainable from the data of this work. One feature concerning semi-conductors that might contribute toward curve displacement is the possible polar effect upon the conductance at low frequencies<sup>34</sup> under high amplification of large impedances. An improvement in physical design of the thermistor could possibly circumvent some undesirable features.

The following summarizes some of the possibilities which may influence the deformation of the cooling curve:

1. The errors involved in transferring the hot liquid from the preheater tube into the Dewar. These may occur through mechanical spattering, or losses due to the vapor-pressure of the material used. The vapor-pressure of ethyl benzene and para-xylene are, respectively, 347 mm. and 325 mm. at 109°C, and change to 257 mm. and 217 mm. at 99°C, respectively.
2. The errors introduced by inadequate or improper stirring are caused by the use of an induction motor controlled by a Variac. Added to this are any variable frictional loads due to changes of bearing surface, and variation of viscosity of the fluids used due to temperature change. The propeller stirrer appeared suitable when tested at lower speeds, but may not have been as efficient

at high speeds.

3. The errors caused by observers and devices other than the thermistor. The time lag error of the amplifier and meters used for null were not measured, but were believed to be less than one second.<sup>24</sup> The time lag caused by the observer actuating the stop watches was variable but usually not greater than that of the amplifier. The stop watches per se behaved erratically, often stopping without perceptible reason, which lead to rejection of several of the unit intervals measured.
4. The chief error appears to be that involving the thermistor. This is most apparent in the bumped portions of Figures 9-15 and 17, but may not be limited exclusively to these areas. Some uncertain effect<sup>34</sup> may be possibly affecting the entire curve displacement. In addition, the thermal time and dissipation constants, which were believed to have been reduced to a small or negligible value, are dependent upon each other as well as the mediums of transfer.

In final retrospect each of these errors can affect the selected dependent variable of time. Except for the first mentioned error above, the effect is a direct in-

fluence on the time. Although the data are not defined enough to say exactly how much a qualitative estimate may be made from the smoothed curves. This seems to indicate some linear relationship between any two substances, but apparently not more than two.

From the foregoing certain improvements and/or recommendations would seem to be desirable. First, a more complete investigation of the thermistor characteristics (i.e. total impedance, power sensitivity, thermal transfer, etc.) under static and dynamic conditions appears necessary. The change to a small thin plate of material, lightly coated with glass, would improve the thermal transfer characteristics. A method of critical selection such as is applied to platinum resistance thermometers might insure the use of desirable elements.

Second, a bridge should be constructed with Evenohm or 1000 Alloy wire in a constant temperature enclosure, using low impedance switches and tested connections. This would permit greater precision and calibration over a wider range for long periods of time.

Third, redesign the present amplifier to enlarge the range of input impedance, sensitivity and stability. This redesigning should be based on the ability to see and amplify, without excessive losses, the moderately short or transient electrical pulses over a direct cur-

rent input.

Fourth, select a wide range time recording device which may be actuated by the amplifier used. A suitable counting device may be necessary to augment the recorder for greater precision and accuracy.

Fifth, an improved calorimeter stirrer and motor might be commercially obtainable for the elimination of any potential errors per se. It might be necessary, however, in higher precision work to calibrate each liquid's viscosity variation with temperature.

Sixth, secure several Dewars constructed more perfectly and completely, paying close attention to small internal mass, geometry of shape, conduction paths, and location of working elements. If properly designed and executed the use of spatter and radiation shields may be unnecessary.

If each of the above is properly attacked and solved the measurement of heat capacities and other thermal transients could be made with better precision and accuracy. As a group project it could possibly be solved in a relatively short time. The temperature sensing device could of itself be a valuable tool to science.

Despite certain deficiencies of materials and equipment, the purposes and intents of this investigation

have been fulfilled. Except for a more desirable accuracy with regard to heat capacities, the overall method, equipment and technique appear to offer vast opportunity for a better understanding of a wide variety of thermal transient measurements and allied processes.

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## BIOGRAPHY

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Mr. Eckel holds membership in the following professional societies: American Chemical Society and the American Association for the Advancement of Science. He is a member of the 3091st Research and Development Group, U. S. Army Reserve.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of the committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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